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(54) **Nonaqueous electrolyte secondary cell and process for production of positive electrode active material therefor.**

(57) The present invention employ a positive electrode comprising an active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe; the numbers of moles of x and y: $0.2 < y \leq 1.3$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn, $0 \leq x < 0.6$; having a hexagonal crystalline structure and the lattice constants, a_0 being in the range of 2.83 to 2.89 Å, c_0 being in the range of 14.15 to 14.31 Å as identified by X-ray diffraction pattern; or where y being in the range of $0.2 < y < 1.0$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn, $0 \leq x < 0.6$; or where y being in the range of $1.0 \leq y \leq 1.3$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn $0 \leq x \leq 0.3$. Particularly. the use of an active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is Mn; the numbers of moles of x and y: $1.0 \leq y \leq 1.3$ and $0 \leq x \leq 0.3$ having the lattice constants: a_0 being in the range of 2.87 to 2.89 Å; c_0 being in the range of 14.15 to 14.25 Å; and the ratio in the diffraction peak intensity of the face (006) to the face (101) indicated by the hexagonal Miller indices, i.e., (006)/(101) being not higher than 0.60; and the magnitude of a unit cell volume being in the range of 101 to 103 Å^3 enables attainment of further enhanced characteristics. The active material represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ is synthesized by employing as starting materials an amount of a compound of divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of at least one nickel compound selected from the group consisting of $Ni(OH)_2$ and $NiCO_3$ corresponding to the number of atomic moles of Ni indicated by 1-x, and an amount of at least one lithium compound selected from the group consisting of Li_2CO_3 and $LiNO_3$ corresponding to the number of atomic moles of Li indicated by y, predrying said starting materials, then subjecting said dried materials to first heat-treatment, passing through normal temperature to produce an intermediate, and subjecting said intermediate to the second heat-treatment at a different temperature than that of the first heat-treatment, with the heat-treatments being conducted in an

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oxidizing atmosphere of air or oxygen.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an improved nonaqueous electrolyte secondary cell using a negative electrode active material such as lithium, lithium alloys, or a carbon material intercalatable with lithium; an electrolyte such as a solution with a nonaqueous solvent; and a positive electrode active material such as a compound oxide containing lithium. More particularly, it relates to a process for producing a positive electrode active material having a hexagonal crystalline structure represented by the general formula, $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe) with lattice constants, a_o = 2.83 to 2.89, c_o = 14.15 to 14.31 Å as identified from X-ray diffraction pattern, and an nonaqueous electrolyte secondary cell using the same.

There has been a vigorous demand of miniaturized secondary cells having a light weight and a high energy density to be used as an electric supply for driving electronic apparatuses such as audio and video appliances and personal computers which have been rapidly rendered portable or cordless in recent years. For this reason, nonaqueous secondary cells, particularly, those using lithium as active material have been strongly expected to be secondary cells having specifically high voltage and high energy density.

Description of the Related Art

As positive electrode active materials to meet the abovementioned demand, there have been proposed layered compounds capable of being intercalated and deintercalated with lithium such as compound oxides containing main components of lithium and transition metals (referred to as lithium compound oxides hereinunder), for example, $Li_{1-x}NiO_2$ with $0 \leq x < 1$, (U.S. Patent No. 4,302,518); $Li_yNi_{2-y}O_2$ (Japanese Patent KOKAI (Laid-open) No. 2-4302518); $Li_yNi_xCo_{1-x}O_2$ with $0 < x \leq 0.75$, $y \leq 1$ (Japanese Patent KOKAI (Laid-open) No. 63--299056). In other materials which have been proposed heretofore there are a compound oxide, $A_xM_yN_zO_2$ where A is an alkali matal, M is a transition metal, and N is at least one of Al, In and Sn with $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$, $0.001 \leq z \leq 0.10$ (Japanese Patent KOKAI (Laid-open) No. 62-90863); and a combination of a major active material, $Li_xM_yN_zO_2$ where M is at least one of transition metals and N is at least one of non-transition metals with $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$, and $0 \leq z \leq 0.10$ and a sub-active material, i.e., a lithium-copper compound oxide (Japanese Patent KOKAI (Laid-open) No. 4-22066).

Synthesis of the positive electrode active materials have been achieved, for example, by heating at temperatures in the range of 600 to 800 °C in air for $Li_yNi_{2-y}O_2$ as disclosed in Japanese Patent KOKAI (Laid-open) No. 2-40861, or by heating at 900 °C for 5 hours in air for $Li_yNiCo_{1-y}O_2$ as disclosed in Japanese Patent KOKAI (Laid-open) No. 3-49155.

Japanese Patent KOKAI (Laid-open) No. 4-181660 proposed that the synthesis of $LiMO_2$ where M is one or more selected from Co, Ni, Fe and Mn should be achieved by heating at temperatures in the range of 600 to 800 °C, preferably by effecting twice the treatment at 800 °C for 6 hours. Alternatively, Japanese Patent KOKAI (Laid-open) No. 4-24831 proposed that the synthesis of $A_xM_yN_zO_2$ where A is an alkali metal, M is a transition metal and N is at least one of Al, In and Sn with $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$, and $0.001 \leq z \leq 0.10$ should be achieved, for example, by heat-treating at 650 °C for 5 hours, and then heat-treating at 850 °C for 12 hours, both in air.

EP 468 942 (A2) proposed that the synthesis of $Li_xNi_{2-(x+y)}M_yO_2$ where $0.8 \leq x \leq 1.0$, and M is any one of Co, Fe, Cr, Ti, Mn, and V, should be accomplished by dispersing nickel hydroxide in a stoichiometric excess of a solution of lithium hydroxide into a slurry, drying the slurry by spray drying, and then heat-treating at a temperature of 600 °C.

With these active materials, development of practical high energy density secondary cells having a discharge voltage on the order of 4 V is being proceeded.

Among these positive electrode active materials, for example, $Li_{1-x}NiO_2$ where $0 \leq x < 1$, (referred to as $LiNiO_2$ hereunder) exhibits a potential of 4 or more relative to lithium, so that its use as a positive electrode active material allows a secondary cell having a high energy density to be realized. The charge and discharge characteristics of the cell, however, are deteriorated with increasing the number of cycles though a discharge capacity of not less than 100 mAh/g can be obtained at initial cycling stage, reaching 65 % of the initial capacity after 50 cycles. Thus, there is a problem of impossibility of achieving a good discharge and discharge cycle property. There is another proposal to produce a cell having an excellent cycle property by synthesizing a compound oxide represented by the aforementioned general formula, but modified by using nickel as transition metal, a part of which is replaced by non-transition metal of indium, aluminum or tin, thereby obtaining an improved positive electrode active material. However, such a lithium

compound oxide as containing an amount of nickel partially replaced by the aforementioned elements tends to reduce the discharge voltage, which adversely affects the characteristics of high voltage and high energy required essentially for the cells.

The charge and discharge capacity of the active materials having this type of layered structure is attributed to an great extent to the crystalline structure of the synthesized active materials. That is, if a desired crystalline active material comprises entirely such a layered crystalline structure as belonging to the space group of $R\bar{3}m$, the maximum capacity in charging and discharging can be achieved. In most cases, however, crystalline domains having a rocksalt structure belonging to the space group of Fm3m are formed in the course of the synthesis. Thus, the domains of the rocksalt structure are produced when an insufficient amount of oxygen is provided in the thermal diffusion of the lithium during the synthesis, or when insufficient thermal vibration or insufficient period of time for the reaction to cause sufficient diffusion of the lithium into the crystalline matrix is bestowed on the lithium.

The presence of such domains dimimishes extremely transfer and diffusion of the lithium ions and the number of receptible sites therefor, resulting in producing a problem of an reduction in the capacity in charging and discharging. For the reasons as described above, it is difficult to produce the active materials having the structure of the space group of $R\bar{3}m$ which allows for a higher capacity.

For example, even if the LiNiO is subjected once or twice to heat-treating at a temperature of 600 to 800 °C for 10 hours in an atmosphere of air, as has been proposed heretofore, one can not obtain a crystalline structure comprising the perfect space group $R\bar{3}m$ as identified by the X-ray diffraction pattern shown in Figure 1. Thus, the ratio in the peak intensity of the face (104) to the face (003) of Miller indices is higher than 1 and similarly the ratio in the peak intensity of the face (102) or (006) to the face (101) as shown in Figure 1 is higher than 1, which are greately different from those of the structure consisting predominantly of the space group $R\bar{3}m$ as shown in Figure 2. In addition, with respect to the lattice constants, crystal lattice parameters, a_0 is 2.885 Å and c_0 is 14.192 Å in Figure 2 while a_0 is 2.905 Å and c_0 is 14.235 Å in Figure 1 indicating an expansion behavior of the lattices.

From the expansion of the lattices and the difference in the peak intensity ratio as described above, it may be considered that the crystalline structure is distorted in the presence of the mixed domains of both the space groups, i.e., the $R\bar{3}m$ and the Fm3m resembling to the former in crystal parameters. Therefore, there is given a problem that the aforementioned synthetic processes can not achieve such active materials capable of providing sufficient capacity in charging and discharging.

SUMMARY OF THE INVENTION

The present invention is to provide a positive electrode active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe; the numbers of moles of x and y: $0.2 < y \leq 1.3$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn $0 \leq x < 0.6$; having a hexagonal crystalline structure and the lattice constants, a_0 being in the range of 2.83 to 2.89 Å , c_0 being in the range of 14.15 to 14.31 as identified by X-ray diffraction pattern; with y being in the range of $0.2 < y < 1.0$, when Me is Ti, V, or Fe, $0 < x < 0.5$, and when Me is Mn, $0 \leq x < 0.6$; with y being in the range of $1.0 \leq y \leq 1.3$, when Me is Ti, V, or Fe, $0 < x < 0.5$, and when Me is Mn, $0 \leq x \leq 0.3$.

Particularly, more excellent characteristics can be obtained by using a positive electrode active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is Mn; the numbers of moles of x and y: $1.0 \leq y \leq 1.3$ and $0 \leq x \leq 0.3$; the lattice constant: a_0 being in the range of 2.87 to 2.89Å and c_0 being in the range of 14.15 to 14.25 Å; the ratio in the peak intensity of the face (006) to the face (101) indicated by the hexagonal Miller indices, i.e., (006)/(101) is not larger than 0.60; and the magnitude of a unit cell volume being in the range of 101 to 103 $Å^3$.

The synthesis of the active materials represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ is performed by preheating the starting materials of an amount of a compound of mainly divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of at least one nickel compound selected from the group consisting of $Ni(OH)_2$ and $NiCO_3$ corresponding to the number of atomic moles of Ni indicated by 1-x, and an amount of a lithium compound corresponding to the number of atomic moles of Li indicated by y, then subjecting to first heat-treatment, passing through cooling stage to produce an intermediate which is subjected to second heat-treatment at a different temperature from that in the first heat-treatment in an oxidizing atmosphere of air or oxygen.

Practically, when the starting material, lithium compound, is $LiNO_3$ hydrate, the synthesis is performed by subjecting to the first heat-treatment consisting of heat-treating at a temperature of 550 to 650 °C for 15 to 20 hours, then passing through normal temperature to produce an intermediate, and thereafter subjecting

to the second heat-treatment of heat-treating at a temperature of 700 to 800 °C for 20 to 25 hours. The X-ray diffraction pattern of an intermediate obtained by the first heat-treatment at a temperature of 550 to 650 °C as above is shown in Figure 3. After the second heat-treatment, there was obtained the X-ray diffraction pattern as shown in Figure 2. On the other hand, when the lithium compound is Li_2CO_3, the synthesis is performed by subjecting to the first heat-treatment consisting of heat-treating at a temperature of 650 to 750 °C for 15 to 20 hours, then passing through normal temperature to produce an intermediate, and thereafter subjecting to the second heat-treatment of heat-treating at a temperature of 800 to 900 °C for 20 to 25 hours. The X-ray diffraction pattern of an intermediate obtained by the first heat-treatment at a temperature of 650 to 750 °C as above is shown in Figure 4. After the second heat-treatment, there was obtained the X-ray diffraction pattern as shown in Figure 2.

Alternatively, when the starting material, lithium compound, is $LiNO_3$ hydrate, the synthesis is carried out by subjecting to the first heat-treatment consisting of heat-treating at a temperature of 700 to 800 °C for 20 to 25 hours, then passing through normal temperature to produce an intermediate, and thereafter subjecting to the second heat-treatment at a temperature of 250 to 350 °C for 10 to 15 hours. The X-ray diffraction pattern of an intermediate obtained by the first heat-treatment at a temperature of 700 to 800 °C as above is shown in Figure 5. After the second heat-treatment, there was obtained the X-ray diffraction pattern as shown in Figure 2.

On the other hand, when the starting material, lithium compound, is $LiCO_3$, the synthesis is accomplished by subjecting to the first heat-treatment consisting of heat-treating at a temperature of 800 to 900 °C for 20 to 25 hours, then passing through normal temperature to produce an intermediate, and thereafter subjecting to the second heat-treatment at a temperature of 250 to 350 °C for 10 to 15 hours. The X-ray diffraction pattern of an intermediate obtained by the first heat-treatment at a temperature of 800 to 900 °C as above is shown in Figure 6. After the second heat-treatment, there was obtained the X-ray diffraction pattern as shown in Figure 2.

The reasons why the active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe, has excellent characteristics may be considered as follows:

Major cationic species, Ni(III) ions determining the lattice structure of, for example, hexagonal $LiNiO_2$ have a low spin type of electronic configuration, on the 3d level of which seven electrons are present. In such oxides, the sixth electron and the seventh one are greatly different in electronic conditions from each other. That is, if the seventh electron is removed, the Fermi level goes down to the lower orbit of two large orbits forming the 3d level so that the electronic conductivity attributable to the upper orbit is reduced and the orbit occupied varies with a variation in spin moment. As a result, the crystal fields contributing to the crystalline structure vary resulting in difficulty of maintaining the original basic hexagonal lattice structure. When the $LiNiO_2$ is used as positive electrode, therefore, repetition of the charging operation, i.e., an oxidation reaction in charging and discharging, causes undesirably gradual deterioration of the crystalline structure with a gradual diminution of its depolarizing ability. This is considered one of factors inhibiting desirable cycle characteristics.

Furthermore, a spinel oxide with Ni, e.g., $LiNi_2O_4$ is considered to be very unstable material finding little practical application owing to difficultly in realization of a higher order oxide state having six electrons on the 3d level at the time of overcharging for the reasons as described above.

According to the present invention, a Ni compound oxide containing transition metals, Ti (the number of nominal valence electrons is four) and V (the number of nominal valence electrons is five) having vacant 3d level is synthesized allowing the transition metal oxide to form a hybrid with the vacant orbitals at lower energy level, whereby a stable crystal field is obtained through exchanging function even at discharging achieving improved cycle characteristics. Moreover, a Ni compound oxide containing Mn (the number of nominal valence electrons being four to three) or Fe (the number of nominal valence electrons being three to two) is synthesized where the transition metal oxide capable of producing a mixed valence condition has partially filled two orbitals of the 3d level and the orbitals of the Ni(III) as described above which are hybridized to form partially filled bands from both metal elements, allowing for the improvement of electronic conductivity as well as for the improvement of cycle characteristics with formation of stable crystal field through exchanging function even at discharging.

Non-transition metals containing Al as have been heretofore proposed have no d orbit, while Sn and In have filled 4d level. Replacement by the former element encounters difficulties in hybridization due to a difference of the orbits from one another and replacement by the latter elements having an electronic configuration at higher energy levels than the 3d level will not be expected to provide a higher operable voltage. However, Ti, V, Mn and Fe having occupied band at the 3d level similarly to Ni will be expected to form almost the same potentials as those of the Ni oxides.

.In this way, the compound oxides where various transition elements are substituted for a part of Ni are capable of forming hexagonal layered structures having lattice constants within specific limitations and their synthesis can be easily conducted.

The synthesis of this type $LiNiO_2$ having the space group $R\bar{3}m$ structure is characterized in that the compound oxide can not be directly produced by heat-treatment from the starting materials, Ni and Li compounds, but through an intermediate to attain the end product as shown in Figure 2. When the starting material, Li compound is a nitrate, the intermediate has a configuration of a NiO compound having a main rhombohedral structure intercalated with Li ions which is produced after the starting Ni compound, e.g., Ni-$(OH)_2$ or $NiCO_3$ underwent ligand exchange to form basic nickel nitrate highly reactive with alkali metals. Alternatively, when the starting material, Li compound is a carbonate, the intermediate has a configuration of a NiO compound having a main rhombohedral structure intercalated with molten Li ions which is produced directly from the starting Ni compound, e.g., $Ni(OH)_2$ or $NiCO_3$. With any one of the Li compounds, the configurations of the intermediates are of a NiO compound having a main rhombohedral structure as can be seen in Figures 3 and 4, and they are produced at about 600 °C for the nitrates, or at 700 °C for the carbonates as identified by means of a high temperature X-ray diffraction apparatus. The variation in the production temperature depending upon the type of Li salt is attributed to a difference in melting point between the former nitrate, around 260 °C and the latter carbonate, around 700 °C as confirmed by means of a differential thermal analysis.

The intermediate may be regarded as a preformer, i.e., so-called precursor, to be transformed into the space group $R\bar{3}m$ structure. That is, it has the identical closest packing structure with oxygen atoms to that of the NiO type having the main rhombohedral structure, and moreover, has Li sites in the vicinity of Ni and O atoms so that it is considered liable to be transformed into the $R\bar{3}m$ structure. The transformation of the intermediate into the $R\bar{3}m$ structure requires a higher temperature than the temperature of the synthesis of the intermediate, and for example, it is achieved at 700 °C or more for the nitrates and at 800 °C or more for the carbonates as identified by means of the high temperature X-ray diffraction apparatus. The temperature of above 950 °C made both the intermediates to have a different crystalline structure from the $R\bar{3}m$ which could not be identified. Therefore, the upper limit of heat-treatment temperature should be 950 °C.

After the intermediates are produced, retention of the heat-treatment temperature for additional time period, or an increase in the heat-treatment temperature were expected to yield an active material having good space group $R\bar{3}m$ structure for the reasons as described above, but did not produce good active materials compared to those obtained by cooling to normal temperature, then mixing and subjecting to the second heat-treatment. This indicates that it is important that diminution of thermal vibration through cooling causes termination of a series of reactions such as excess atomic transfer and transition, correcting the arrangement of metals and oxygen atoms and preventing partial transformation of the structure into the $R\bar{3}m$ structure, and that the bulk of an active material is homogenized by milling and mixing the sintered product. It is important, therefore, conducting the first heat-treatment, cooling to normal temperature to produce an intermediate and then conducting again heat-treatment. In contrast, when the space group $R\bar{3}m$ structure is to be formed in the intermediate, NiO compound intercalated with Li, without cooling to normal temperature, it is difficult to achieve certainly good characteristics as described above.

The achieved materials which are produced by one-step heat-treatment intending to directly form the $R\bar{3}m$ structure and which can not achieve good characteristics may be regarded as one of intermediates other than the aforementioned ones and treated to have good $R\bar{3}m$ structure by the following procedure. That is, the intermediate having imperfect $R\bar{3}m$ structure is milled and mixed as a post-step, and again subjected to heat-treatment effecting rearrangement of metal and oxygen atoms, whereby non-uniformity of the concentration of Li in the surface layer of the bulk active material can be remedied. The reheating temperature in this case should be desirably lower than the synthesis temperature for the intermediate. All the heat-treating steps are commonly performed in an oxidizing atmosphere. The Ni oxides (the number of nominal atomic valence of three) are said to have 0 to 1 electron (as one-electron reaction) on the e_g orbit forming an upper band of the 3d level so that they have essentially less tendency to cause electron affinity reaction. In the course of intercalation of Li, the electron affinity reaction must inevitably occur so that the intercalation of Li into the matrix becomes difficult unless there is present a significant amount of ligand oxygen atoms.

Therefore, it is important to conduct the synthesis in an oxidizing atmosphere, preferably in an atmosphere of oxygen.

The use of the active materials represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$, produced by two step heat-treating process as described above enables attainment of lithium secondary cells having good cycle characteristics and higher

capacity..

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a X-ray diffraction pattern of the positive electrode active material obtained by the conventional synthesis.

Figure 2 is a X-ray diffraction pattern of the $Li_yNi_{1-x}Mn_xO_2$ having the space group R$\bar{3}$m structure contemplated by the present invention.

Figure 3 is a X-ray diffraction pattern of the intermediate obtained from the starting material, $LiNO_3$ when the temperature of the first heat-treatment was in the range of 550 to 650 °C.

Figure 4 is a X-ray diffraction pattern of the intermediate obtained from the starting material, Li_2CO_3 when the temperature of the first heat-treatment was in the range of 650 to 750 °C.

Figure 5 is a X-ray diffraction pattern of the intermediate obtained from the starting material, $LiNO_3$ when the temperature of the first heat-treatment was in the range of 700 to 800 °C.

Figure 6 is a X-ray diffraction pattern of the intermediate obtained from the starting material, Li_2CO_3 when the temperature of the first heat-treatment was in the range of 800 to 900 °C.

Figure 7 is a heat-treating temperature vs. heat-treating time plot for the synthesis of the intermediate in Example 2 according to the present invention.

Figure 8 is a heat-treating temperature vs. heat-treating time plot for the production of an end product having the R$\bar{3}$m structure from the intermediate in Example 2.

Figure 9 is a X-ray diffraction pattern of Comparative sample.

Figure 10 is a schematic vertical cross-sectional view of the cylindrical cell according to an embodiment of the present invention.

Figure 11 shows lattice constant plots of the hexagonal $Li_yNi_{1-x}Me_xO_2$ where Me is Ti, or V with y = 0.1 and 1.0.

Figure 12 shows lattice constant plots of the hexagonal $Li_yNi_{1-x}Me_xO_2$ where Me is Ti, or V with y = 1.3 and 1.5.

Figure 13 shows lattice constant plots of the hexagonal $Li_yNi_{1-x}Me_xO_2$ where Me is Mn, or Fe with y = 0.1 and 1.0.

Figure 14 shows lattice constant plots of the hexagonal $Li_yNi_{1-x}Me_xO_2$ where Me is Mn, or Fe with y = 1.3 and 1.5.

Figure 15 shows plots of peak electric current at cathode as a function of x of the $Li_yNi_{1-x}Me_xO_2$.

Figure 16 shows plots of peak electric current at cathode as a function of y of the $Li_yNi_{1-x}Me_xO_2$.

Figure 17 is a graph showing the average voltage variation width at peak electric current at cathode with varying Me.

Figure 18 is a plot showing the relationship between the peak electric current at cathode and the ratio of X-ray diffraction peak intensities I = (006)/(101).

Figure 19 is a plot showing the relationship between the lattice constant c_0 and the ratio of X-ray diffraction peak intensities I = (006)/(101).

Figure 20 is a plot showing the relationship between the lattice constant a_0 and the ratio of X-ray diffraction peak intensities I = (006)/(101).

Figure 21 is a plot showing the relationship between the hexagonal lattice unit volume and the ratio of X-ray diffraction peak intensities I = (006)/(101).

Figure 22 is a plot showing the relationship between the heat-treating temperature and the heat-treating time employed for the synthesis of the intermediate in Example 2.

Figure 23 is a plot showing the relationship between the heat-treating temperature and the heat-treating time for producing the end product having the R$\bar{3}$m structure from the intermediate in Example 2.

Figure 24 is a plot showing the relationship between the heat-treating temperature and the firing time employed for the synthesis of the intermediate in Example 3.

Figure 25 is a plot showing the relationship between the heat-treating temperature and the heat-treating time for producing the end product having the R$\bar{3}$m structure from the intermediate in Example 2.

Figure 26 is a plot showing the relationship between the heat-treating temperature and the heat-treating time employed for the synthesis of the intermediate in Example 4.

Figure 27 is a plot showing the relationship between the heat-treating temperature and the heat-treating time for producing the end product having the R$\bar{3}$m structure from the intermediate in Example 4.

Figure 28 is a X-ray diffraction pattern of the positive electrode active material obtained by the synthesis in Comparative Example.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Practical process for synthesizing the active materials according to the present invention and the use thereof in cells as positive electrode materials will be in detail described hereunder. The synthesis of the $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe, is performed by mixing prime materials Li_2O and $Ni(OH)_2$ with TiO_2 when the substituent transition element is Ti, or with $MnCO_3$ when it is Mn, or with α or β -Fe_2O_3 when it is Fe, in a predetermined compositional proportion, then shaping the mixture into tablets and heat-treating the tablets at a temperature of 850 °C for 20 hours in air. Preferably, the synthesis of the $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ is performed by using $Ni(OH)_2$, Li_2CO_3, and $MnCO_3$ as starting materials.

The active materials as above have been synthesized by various processes. Those having a value of x over 0.3 tend to have a crystalline structure exhibiting a broader peak, i.e., lower crystallinity than those having a value of x not higher than 0.3. With x being 0.4, a Mn spinel peak becomes to appear which may cause a conceivable reduction in charge and discharge capacity. If the y determining the amount of Li is lower than 1.0, the diffraction peak intensity of the face (101) relative to the face (006) of the $R\bar{3}m$ structure becomes higher than 1.0 as discussed previously with an increase of the Fm3m domain, resulting in an reduction in charge and discharge capacity. Conversely, if the y is over 1.3, an excess of Li ions is present in the surface layer of the active material so that after an electrode plate is formed, it is susceptible to corrosion.

Therefore, the $Li_yNi_{1-x}Mn_xO_2$ should preferably have a composition with $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$. A process for synthesis thereof will be described under.

50 g of the starting materials prepared by mixing in a predetermined proportion was placed in an aluminum vessel and preliminarily dried at a temperature of 150 °C for 15 hours to remove adsorbed moisture, then subjecting to the first heat-treatment of heat-treating at 600 to 800 °C for 10 to 25 hours in an atmosphere of oxygen, and cooling to normal temperature to produce an intermediate. The conditions for producing the intermediate having the same crystalline structure as that shown in Figure 4 were selected based on the analysis of the X-ray diffraction pattern.

Figure 7 is a plot of the occurrence of a production of the intermediate under the conditions of each heat-treating temperature and time. In the analysis of the X-ray diffraction pattern, a case where any materials having other crystalline structure than that of the intermediate such as unreacted Li compounds were included was considered unsuitable and eliminated from the plot.

It can be seen from Figure 7 that the production of the intermediate is possible under the conditions of a heat-treating temperature in the range of 650 to 750 °C and a heat-treating time in the range of 15 to 25 hours. A temperature of 600 °C resulted in remaining unreacted Li compounds to be observed, while a temperature of 800 °C resulted in the presence of a part of the $R\bar{3}m$ structure to be observed indicating these conditions unsuitable. Even if the heat-treating temperatures are in the region making the production of the intermediate possible, a heat-treating time of 10 hours resulted in remaining unreacted Li compounds. In contrast, a heat-treating time of 25 hours was already enough for the heat-treatment and could not achieve any further improvement compared to the case of 20 hours so that the 20 hours may be considered sufficient to be the upper limit of the heat-treating time. From the forgoing, the firing conditions for the production of the intermediate should be preferably a heat-treating temperature in the range of 650 to 750 °C and a firing time in the range of 15 to 20 hours.

Next, an intermediate produced within the aforementioned conditions, for example, by heat-treating at 700 °C for 15 hours was well ground into -100 mesh particles which were subjected to the second heat-treatment. After the second heat-treatment of heat-treating at a temperature of 750 to 950 °C for 15 to 30 hours in an atmosphere of oxygen, the particles were cooled to normal temperature. The conditions for production of the end product having the space group $R\bar{3}m$ of the identical crystalline structure to that shown in Figure 2 were selected based on the analysis of the X-ray diffraction pattern. Figure 8 is a plot of the occurrence of a production of the intermediate under the conditions of each heat-treating temperature and time. In the analysis of the X-ray diffraction pattern, a case where any material exhibiting other crystalline structure than the $R\bar{3}m$ of the end product, e.g., rocksalt domains having the space group Fm3m and a part of the intermediate produced by the first heat-treatment were left was considered unsuitable and eliminated from the plot.

It can be seen from Figure 8 that the production of the end product is possible under the conditions of a heat-treating temperature in the range of 800 to 900 °C and a heat-treating time in the range of 20 to 25 hours. A temperature of 750 °C resulted in a remaining part of the unreacted intermediate which had been produced by the first heat-treatment, while a temperature of 950 °C resulted in the presence of a part of the $R\bar{3}m$ structure to be observed indicating these conditions unsuitable. Even if the heat-treating

An electrolyte to be used was prepared by dissolving 1 mol/l of lithium perchlorate into an equivolume mixture of propylene carbonate and ethylene carbonate as solvent. This electrolyte was poured in a predetermined amount into cells which were sealed and used for the test. The test was conducted at room temperature at a constant current in charging and discharging under the conditions of a discharging current of 100 mA, a terminal charging voltage of 4.1 V and a terminal discharging voltage of 3.0 V up to 50 cycles.

As a result, the similar active materials as those obtained by the synthesis according to the present invention reached about 57 % of the initial capacity, while the contrast sample 1 with x = 1 reached about 50 % of the initial capacity. The active materials with x = 0.2 among those obtained by the synthesis according to the present invention reached about 85 %. Therefore, it is believed that the use of the synthetic process of the present invention with attainment of the compound atomic valence state containing Mn makes it possible to achieve a higher capacity and enhanced cycle characteristics, and hence effects of improving the characteristics.

Figure 10 shows one of the cylindrical cells where 1 designates a cell case made of a stainless steel resistant to organic electrolyte, 2 does a seal plate equipped with a safty valve, and 3 does an insulating packing. 4 designates a combination of positive and negative electrode plates with a separator being interposed therebetween which is rolled in a spiral form and received in a case. A positive electrode lead 5 is attached to the positive electrode and connected to the seal plate 2, while a negative electrode lead 6 is attached to the bottom of the cell case 1. A insulating ring 7 is provided on each of the top and the bottom of the combination of the electrodes.

Example 1

Lattice constants of compound oxides having a composition, $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe, with y being 0.1, 1.0, 1.3 and 1.5 and with varying x were calculated based on X-ray diffraction patterns. The results are shown in Figures 11 to 14.

As can be seen from these Figures, the hexagonal compound oxides represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe, have lattice constants of a_0 in the range of 2.83 to 2.89 and c_0 in the range of 14.15 to 14.31. In order to select optimum compositions for the positive electrode active materials, peak values of cathode response currents and a voltage width corresponding to the half width of a current wave peak were evaluated by conducting a potential scanning across the sample electrodes. A sample electrode arrangement was made with a composite which was made by filling an electrode formulation consisting of a mixture of a positive electrode active material, acetylene black and fluorinated resin adhesive in a ratio of 7 : 1.5 : 1.5 by weight into a 8 cm^2 of electrode; a counter electrode of lithium metal; and a reference electrode of another lithium metal. As an electrolyte, there was used a solution which was prepared by dissolving 1 mol/l of $LiPF_6$ into a mixed solvent of ethylene carbonate and diethylene carbonate in a ratio of 1 : 1. The scanning was conducted at a speed of 2 mV/s and at a voltage in the range of 3.1 V to 4.5 V. With y = 1.0, the peak value of the cathode response current for each value of the x is shown in Figure 15. As can be seen from the Figure 15, the hexagonal compound oxides represented by the general formula, $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe, are good with Ti, V and Fe ($0 < x < 0.5$), and with Mn ($0 \leq x < 0.6$). Particularly, with Mn ($0 \leq x \leq 0.3$), very excellent results were obtained for the peak current value.

Selecting x = 0.2 among the values of x resulting in the hexagonal materials having good characteristics, the peak values of the cathode response current with varying y are shown in Figure 16. As can be seen from the Figure 16, when y is 0.2 to 1.5, a characteristic exhibiting 70 mA or more can be attained and the range of 1.0 to 1.3 is most preferable. When y was 1.5, a good result was obtained. However, since an excess lithium unreacted was still left in the positive electrode, y is preferably 1.3. The samples synthesized with y = 0.1 resulted in a reduction in cathode peak current to one half. From this fact, the synthesis should be accomplished under preferred conditions with the lower limit of y being 0.2, preferably 1.0 or higher and the upper limit being 1.3.

An average value of voltage width is shown in Figure 17. It can be found from this Figure that when the x value is in the aforementioned range, the positive electrode active materials function as those having a high voltage of about 4 V because the average value of voltage width varies from a lower limit of 3.85 V to an upper limit of 4.03 V.

From the results as above, it is believed for hexagonal materials that the synthesis conditions should be preferably in the range of $0.2 < y \leq 1.3$, and when the substituent transition element is Mn, more preferably be $1.0 \leq y \leq 1.3$. Taking account of the results of the measurement of cathode peak current as described above, the crystalline materials synthesized with x and y being in the specified ranges had lattice constants of a_0 in the range of 2.83 to 2.89 and c_0 in the range of 14.15 to 14.31 and specifically when the substituent

elemtent is Mn, a_0 in the range of 2.87 to 2.89 and c_0 in the range of 14.15 to 14.25 corresponding to the composition with $0 \leq x \leq 0.3$. In this region, further improved characteristics may be achieved.

Next, the relationship between the crystalline structure and the composition will be discussed under.

The hexagonal materials represented by the formula, $Li_yNi_{1-x}Me_xO_2$ have a crystalline structure belonging to the space group $R\bar{3}m$. Dependency of the crystalline structure on the y value has been a number of workers as described, for example, by J.B. Goodenough et al in J. Phys. Chem. Solids, 5 (1958) 107 where the dependency of the cell volume of the rhombohedral structure of the pure nickel hexagonal system upon the y value follows almost a negative linear function, that is, the cell volume decreases with increasing the y value. J.R. Dahn et al describe in Solid State Ionics 44 (1990) 87 that the ratio in diffraction peak intensity of the face (006) to the face (101) of Miller indices as identified from the X-ray diffraction pattern of this crystalline structure (the ratio is designated I hereunder) was calculated and concluded taking into consideration the results of Goodenough et al that the I and the rhombohedral cell volume may be placed on an increase function and conversely the I and the y value may be expressed by a negative function. This is such that the I decreases with increasing the y value. In the literature, with $y = 1$, the I is about 0.5.

From the fact as above, the ratio in diffraction peak intensity I can be regarded as an important parameter indicating the character of crystalline structure. The present inventers have made an intensive research to find correlations of the reported results with the effects on electrochemical properties and even with the starting materials for the synthesis.

For example, a sample was synthesized by preparing a mixture of major materials, Li_2CO_3, $Ni(OH)_2$, and $MnCO_3$ in a predetermined proportion as starting materials and heat-treating at 850 °C for 20 hours in an atmosphere of air and evaluated for the relationship between the I and the cathode peak current value. The results are shown in Figure 18. As can be seen from Figure 18, as the I of the sample is increased, the cathode peak current value decreases indicating deactivation. When I is 0.6 or less, a current value not less than 80 mA is obtained indicating active state.

Next, the relationship between the I and the lattice constant is shown in Figures 19 and 20. It can be found from both Figures that as the I increases, the lattice constants a_0 and c_0 are rapidly increased. In the range of I not higher than 0.6 where a cathode peak current value not less than 80 mA is obtained as indicated in Figure 18, the lattice constants are $2.87 < a_0 < 2.89$, and $14.15 < c_0 < 14.25$, which provides clearly a correlation of the electrochemical activity with the crystalline parameters. That is, there can be obtained an information that when the compound oxides synthesized satisfy the condition of the ratio in diffraction peak intensity $(006)/(101) < 0.6$, they are electrochemically active and have the lattice constants being in the ranges of $2.87 < a_0 < 2.89$, and $14.15 < c_0 < 14.25$. The lower limits of a_0 and c_0 were determined based on this fact since any sample exhibiting a_0 of 2.87 or less and c_0 of 14.15 or less could not be experimentally synthesized. Chemical analysis also indicated that when the I was 0.6, the y value was 1.02.

Next, the relationship between the hexagonal unit cell volume and the I value is shown in Figure 21. The unit cell volume was calculated based on the lattice constants. As a result, with the unit volume being in the range of 101 to 103 Å^3, the I value was not higher than 0.6 indicating the possibility of being electrochemically active. Any sample having a unit cell volume of 101 Å^3 or less could not experimentally synthesized.

Example 2

The synthesis of the $Li_yNi_{1-x}Mn_xO_2$ is performed by mixing major materials, $Ni(OH)_2$ or $NiCO_3$, $LiNO_3$ hydrate or Li_2CO_3, and a divalent manganese compound such as $MnCO_3$ in a predetermined compositional proportion, then preliminarily drying at a temperature of 150 °C for 15 hours to remove adsorbed moisture from the starting materials, then subjecting to the first heat-treatment, cooling to normal temperature, milling and mixing, and then subjecting the resultant mixture to the second heat-treatment at different temperatures than those of the first heat-treatment. The heat-treatment should be performed in an oxidizing atmosphere, preferably in an atmosphere of oxygen.

The composition, $Li_yNi_{1-x}Mn_xO_2$ should preferably be under the conditions of $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$. However, the examples below employed the basic composition where $x = 0$ and 0.2, and $y = 1.0$ and 1.1. Each synthesis will be described in detail hereunder.

In the following description, as starting materials, there were employed $Ni(OH)_2$, $LiNO_3$ and $MnCO_3$. 50 g of the starting materials prepared by mixing in a predetermined proportion was placed in an aluminum vessel, then preliminarily dried at a temperature of 150 °C for 15 hours to remove adsorbed moisture from the starting materials, subjecting to the first heat-treatment of heat-treating at a temperature of 500 to 700

°C for 10 to 25 hours in an atmosphere of oxygen, and then cooling to normal temperature to produce an intermediate. The conditions for producing the intermediate having the same crystalline structure as that shown in Figure 6 were selected based on the analysis of the X-ray diffraction pattern.

Figure 22 is a plot of the occurrence of a production of the intermediate under the conditions of each heat-treating temperature and time. In the analysis of the X-ray diffraction pattern, a case where any materials having other crystalline structure than that of the intermediate such as unreacted Li compounds are included was considered unsuitable and eliminated from the plot. It can be seen from Figure 22 that the production of the intermediate is possible under the conditions of a heat-treating temperature in the range of 550 to 650 °C and a heat-treating time in the range of 15 to 25 hours. A temperature of 500 °C resulted in remaining unreacted Li compounds to be observed, while a temperature of 700 °C resulted in the presence of a part of the $R\bar{3}m$ structure to be observed indicating these conditions unsuitable. Even if the heat-treating temperatures are in the region making the production of the intermediate possible, a heat-treating time of 10 hours resulted in remaining unreacted Li compounds. In contrast, a heat-treating time of 25 hours was already enough for the heat-treatment and could not achieve any further improvement compared to the case of 20 hours so that the 20 hours may be considered sufficient to be the upper limit of the heat-treating time. From the forgoing, the heat-treatment conditions for the production of the intermediate should be preferably a heat-treating temperature in the range of 650 to 750 °C and a heat-treating time in the range of 15 to 20 hours.

Next, an intermediate produced within the aforementioned conditions, for example, by heat-treating at 600 °C for 15 hours was well ground into -100 mesh particles which were subjected to the second heat-treatment. After the second heat-treatment of heat-treating at a temperature of 650 to 850 °C for 15 to 30 hours in an atmosphere of oxygen, the particles were cooled to normal temperature. The conditions for production of the end product having the space group $R\bar{3}m$ of the identical crystalline structure to that shown in Figure 2 were selected based on the analysis of the X-ray diffraction pattern. Figure 23 is a plot of the occurrence of a production of the intermediate under the conditions of each heat-treating temperature and time. In the analysis of the X-ray diffraction pattern, a case where any material indicating a different crystalline structure from the $R\bar{3}m$ of the end product, e.g., rocksalt domains having the space group Fm3m and a part of the intermediate produced by the first heat-treatment was left was considered unsuitable and eliminated from the plot.

It can be seen from Figure 23 that the production of the end product is possible under the conditions of a heat-treating temperature in the range of 700 to 800 °C and a heat-treating time in the range of 20 to 25 hours. A temperature of 650 °C resulted in a remaining part of the unreacted intermediate which had been produced by the first heat-treatment, while a temperature of 850 °C resulted in the presence of a part of the $R\bar{3}m$ structure to be observed indicating these conditions unsuitable. Even if the heat-treating temperatures are in the region making the production of the end product possible, a heat-treating time of 15 hours resulted in the remaining unreacted intermediate. Contrary, a heat-treating time of 30 hours was already enough for the heat-treatment and could achieve almost no more than in the case of 25 hours so that the 25 hours may be considered sufficient to be the upper limit of the heat-treating time. From the forgoing, the heat-treatment conditions for the synthesis of the end product having the $R\bar{3}m$ structure as the second heat-treatment after the formation of the intermediate should be preferably a heat-treating temperature in the range of 800 to 900 °C and a heat-treating time in the range of 20 to 25 hours in an atmosphere of oxygen.

Alternatively, the use of $NiCO_3$ as starting material as well as the use of air as heat-treatment atmosphere produced the identical results. In this example 2, the intermediate which had been produced by heat-treating at a temperature of 600 °C for 15 hours was employed, though those produced at heat-treating temperatures in the range of 550 to 650 °C for a heat-treating time period in the range of 15 to 20 hours could be employed to achieve effective results by the second heat-treatment.

Example 3

In the following description, as starting materials, there were employed $Ni(OH)_2$, $LiNO_3$ and MnO_2.

50 g of the starting materials prepared by mixing in a predetermined proportion was placed in an aluminum vessel, then preliminarily dried at a temperature of 150 °C for 15 hours to remove adsorbed moisture from the starting materials, subjected to the first heat-treatment of heat-treating at a temperature of 650 to 850 °C for 15 to 30 hours in an atmosphere of oxygen, and then cooled to normal temperature to produce an intermediate. The conditions for producing the intermediate having an imperfect space group $R\bar{3}m$ structure of the same crystalline structure of as that shown in Figure 5 were selected based on the analysis of the X-ray diffraction pattern.

Figure 24 is a plot of the occurrence of a production of the intermediate under the conditions of each heat-treating temperature and time. In the analysis of the X-ray diffraction pattern, a case where any materials having other crystalline structure than that of the intermediate such as remaining NiO oxide intermediate as described in Example 2 were left or domains of the space group Fm3m structure were present was considered unsuitable and eliminated from the plot.

It can be seen from Figure 24 that the production of the intermediate is possible under the conditions of a heat-treating temperature in the range of 700 to 800 °C and a heat-treating time in the range of 15 to 30 hours. A temperature of 650 °C resulted in the presence of the NiO oxide intermediate as described in Example 2 to be observed, while a temperature of 650 °C resulted in the presence of a part of the Fm3m structure to be observed indicating these conditions unsuitable. Even if the heat-treating temperatures are in the region making the production of the $R\bar{3}m$ structure possible, a heat-treating time of 15 hours resulted in remaining the NiO oxide intermediate. In contrast, a heat-treating time of 30 hours was already enough for the heat-treatment and could not achieve any further improvement compared to the case of 20 hours so that the 20 hours may be considered sufficient to be the upper limit of the heat-treating time.

From the forgoing, the heat-treatment conditions for the production of the intermediate should be preferably a heat-treating temperature in the range of 700 to 800 °C and a heat-treating time in the range of 20 to 25 hours.

Next, an intermediate produced within the aforementioned conditions, for example, by heat-treating at 750 °C for 25 hours was well ground into -100 mesh particles which were subjected to the second heat-treatment. After the second heat-treatment of heat-treating at a temperature of 200 to 400 °C for 5 to 20 hours in an atmosphere of oxygen, the particles were cooled to normal temperature. The conditions for production of the end product having the space group $R\bar{3}m$ of the identical crystalline structure to that shown in Figure 2 were selected based on the analysis of the X-ray diffraction pattern.

As the intermediate obtained in this Example had the space group $R\bar{3}m$ structure almost entirly formed already, the base for the selection was the crystal parameter that the ratio in diffraction peak intensity of the face (006) to the face (101) of Miller indices in Figure 2 was not higher than 0.40 which was much smaller than 0.06.

Figure 25 is a plot of the crystal parameter under the conditions that the ratio in diffraction peak intensity of the face (006) to the face (101) was not higher than 0.40 depending upon each heat-treating temperature and time. As can be seen from the Figure, the crystal parameter for the end product can be achieved under the conditions of a heat-treating temperature in the range of 250 to 350 °C and a heat-treating time in the range of 10 to 15 hours. A temperature of 200 °C was not expected to achieve sufficient crystal growth, and conversely a temperature of 400 °C tended to increase again the crystal parameter over 0.4, which was supposed attributable to a rearrangement disorder in the crystal.

Even if the heat-treating temperatures are in the region making the production of the $R\bar{3}m$ structure possible, a heat-treating time of 5 hours was not expected to give sufficient crystal growth, while a heat-treating time of 20 hours was already enough for the heat-treatment and could achieve almost no more than in the case of 15 hours so that the 15 hours may be considered sufficient to be the upper limit of the heat-treating time.

From the forgoing, the heat-treatment conditions for the synthesis of the end product having the $R\bar{3}m$ structure as the second heat-treatment after the formation of the intermediate should be preferably a heat-treating temperature in the range of 250 to 350 °C and a heat-treating time in the range of 10 to 15 hours in an atmosphere of oxygen.

Alternatively, the use of $NiCO_3$ as starting material as well as the use of air as heat-treating atmosphere produced the identical results. In this example 3, the intermediate which had been produced by heat-treating at a temperature of 750 °C for 25 hours was employed, though those produced at heat-treating temperatures in the range of 700 to 800 °C for a heat-treating time period in the range of 20 to 25 hours could be employed to achieve effective results by the second heat-treatment.

Example 4

In the following description, as starting materials, there were employed $Ni(OH)_2$, Li_2CO_3 and $MnCO_3$.

50 g of the starting materials prepared by mixing in a predetermined proportion was placed in an aluminum vessel, then preliminarily dried at a temperature of 150 °C for 15 hours to remove adsorbed moisture from the starting materials, subjected to the first heat-treatment of heat-treating at a temperature of 750 to 950 °C for 15 to 30 hours in an atmosphere of oxygen, and then cools to normal temperature to produce an intermediate. The conditions for producing the intermediate having an imperfect space group $R\bar{3}m$ structure of the same crystalline structure as that shown in Figure 6 were selected based on the

analysis of the X-ray diffraction pattern.

Figure 26 is a plot of the occurrence of a production of the intermediate under the conditions of each combination of heat-treating temperature and time. In the analysis of the X-ray diffraction pattern, a case where any materials having other crystalline structure than that of the intermediate such as remaining NiO oxide intermediate were left or domains of the space group Fm3m structure were present was considered unsuitable and eliminated from the plot.

It can be seen from Figure 26 that the production of the intermediate is possible under the conditions of a heat-treating temperature in the range of 800 to 900 °C and a heat-treating time in the range of 20 to 30 hours. A temperature of 750 °C resulted in the presence of the NiO oxide intermediate as described in Example 2 to be observed, while a temperature of 950 °C resulted in the presence of a part of the Fm3m structure to be observed indicating these conditions unsuitable. Even if the heat-treating temperatures are in the region making the production of the $R\bar{3}m$ structure possible, a heat-treating time of 15 hours resulted in remaining the NiO oxide intermediate. In contrast, a heat-treating time of 30 hours was already enough for the heat-treatment and could not achieve any further improvement compared to the case of 20 hours so that the 25 hours may be considered sufficient to be the upper limit of the heat-treating time.

From the forgoing, the heat-treatment conditions for the production of the intermediate should be preferably a heat-treating temperature in the range of 800 to 900 °C and a heat-treating time in the range of 20 to 25 hours.

Next, an intermediate produced within the aforementioned conditions, for example, by heat-treating at 750 °C for 25 hours was well ground into -100 mesh particles which were subjected to the second heat-treatment. After the second heat-treatment of heat-treating at a temperature of 200 to 400 °C for 5 to 20 hours in an atmosphere of oxygen, the particles were cooled to normal temperature. The conditions for production of the end product having the space group $R\bar{3}m$ of the identical crystalline structure to that shown in Figure 2 were selected based on the analysis of the X-ray diffraction pattern.

As the intermediate obtained in this Example had the space group $R\bar{3}m$ structure almost entirely formed already, the base for the selection to be used was the crystal parameter that the ratio in diffraction peak intensity of the face (006) to the face (101) of Miller indices in Figure 2 was not higher than 0.40.

Figure 27 is a plot of the crystal parameter under the conditions that the ratio in diffraction peak intensity of the face (006) to the face (101) was not higher than 0.40 depending upon each combination of heat-treating temperature and time. As can be seen from the Figure, the crystal parameter for the end product can be attained under the conditions of a heat-treating temperature in the range of 250 to 350 °C and a heat-treating time in the range of 10 to 15 hours. A temperature of 200 °C was not expected to achieve sufficient crystal growth, and conversely a temperature of 400 °C tended to increase again the crystal parameter over 0.4, which was supposed attributable to a rearrangement disorder in the crystal.

Even if the heat-treating temperatures are in the region making the production of the $R\bar{3}m$ structure possible, a heat-treating time of 5 hours was not expected to give sufficient crystal growth, while a heat-treating time of 20 hours was already enough for the heat-treatment and could achieve almost no more than in the case of 15 hours so that the 15 hours may be considered sufficient to be the upper limit of the heat-treating time.

From the forgoing, the heat-treatment conditions for the synthesis of the end product having the $R\bar{3}m$ structure as the second heat-treatment after the formation of the intermediate should be preferably a heat-treating temperature in the range of 250 to 350 °C and a heat-treating time in the range of 10 to 15 hours in an atmosphere of oxygen.

Alternatively, the use of $NiCO_3$ as starting material as well as the use of air as heat-treatment atmosphere produced the identical results. In this example 4, the intermediate which had been produced by heat-treating at a temperature of 850 °C for 25 hours was employed, though those produced at heat-treating temperatures in the range of 800 to 900 °C for a heat-treating time period in the range of 20 to 25 hours could be employed to achieve effective results by the second heat-treatment.

Comparative Example

Description will be made under about a case where $Ni(OH)_2$, Li_2CO_3 and $MnCO_3$ were employed as starting materials.

50 g of the starting materials prepared by mixing in a predetermined proportion was placed in an aluminum vessel, then preliminarily dried at a temperature of 150 °C for 15 hours to remove adsorbed moisture from the starting materials, fired at a temperature of 750 °C for 10 hours in an atmosphere of oxygen, cooled to normal temperature, ground, mixed and again fired at a temperature of 750 °C for 10 hours in an atmosphere of oxygen. X-ray diffraction pattern of the resulting product is shown in Figure 28.

No crystalline product having good $R\bar{3}m$ structure was obtained.

Example 5

The discharge capacities of the samples produced in Examples as described above and the sample of the Comparative Example after 10 cycles of charging and discharging are shown in Table 2. The active materials were of the composition, $Li_yNi_{1-x}Mn_xO_2$ where x = 0 and 0.2, and y = 1.0 and 1.1. The sample obtaind in Example 2 was an active material which was produced by heat-treating the starting materials at 600 •C for 15 hours to produce an intermediate and post-heat-treating the intermediate at 750 •C for 25 hours. The sample produced by the most preferred process of the present invention was an active material which was produced by heat-treating the starting materials at 700 •C for 15 hours to produce an intermediate and post-heat-treating the intermediate at 850 •C for 25 hours. The sample obtaind in Example 3 was an active material which was produced by heat-treating the starting materials at 750 •C for 25 hours to produce an intermediate and post-heat-treating the intermediate at 350 •C for 15 hours. The sample obtaind in Example 4 was an active material which was produced by heat-treating the starting materials at 850 •C for 25 hours to produce an intermediate and post-heat-treating the intermediate at 350 •C for 15 hours.

Table 2

Sample	x	y	Capacity(mAh/g)
Example 2	0	1.0	152
		1.1	153
	0.2	1.0	148
		1.1	155
Most preferred process	0	1.0	150
		1.1	151
	0.2	1.0	145
		1.1	151
Example 3	0	1.0	149
		1.1	152
	0.2	1.0	144
		1.1	147
Example 4	0	1.0	148
		1.1	152
	0.2	1.0	145
		1.1	149
Contrast 1	0	1.0	129
		1.1	137
	0.2	1.0	120
		1.1	131
Comparative Example	0	1.0	132
		1.1	135
	0.2	1.0	128
		1.1	135

As can be seen from table 2, the use of the synthesis process according to the present invention allows an enhancement of the discharge capacity from the conventional range of 120 to 130 mAh/g to the range of 140 to 150 mAh/g.

Claims

1. A nonaqueous secondary cell comprising:
   a positive electrode comprising an active material represented by the general formula:

$Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe; the numbers of moles of x and y: $0.2 < y \leq 1.3$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn, $0 \leq x < 0.6$; having a hexagonal crystalline structure and the lattice constants, a_0 being in the range of 2.83 to 2.89 Å, c_0 being in the range of 14.15 to 14.31 Å as identified by X-ray diffraction pattern;
a negative electrode of lithium, a lithium alloy, or a carbon material intercalated with lithium; and
a nonaqueous electrolyte.

2. A nonaqueous secondary cell comprising:
a positive electrode comprising an active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe; the numbers of moles of x and y: $0.2 < y < 1.0$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn, $0 \leq x < 0.6$; having a hexagonal crystalline structure and the lattice constants, a_0 being in the range of 2.83 to 2.88 Å, c_0 being in the range of 14.15 to 14.31 Å as identified by X-ray diffraction pattern;
a negative electrode of lithium, a lithium alloy, or a carbon material intercalated with lithium; and
a nonaqueous electrolyte.

3. A nonaqueous secondary cell comprising:
a positive electrode comprising an active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is any one of Ti, V, Mn and Fe; the numbers of moles of x and y: $1.0 \leq y \leq 1.3$; when Me is Ti, V, or Fe, $0 < x < 0.5$; and when Me is Mn, $0 \leq x \leq 0.4$; having a hexagonal crystalline structure and the lattice constants, a_0 being in the range of 2.83 to 2.89 Å, c_0 being in the range of 14.15 to 14.31 Å as identified by X-ray diffraction pattern;
a negative electrode of lithium, a lithium alloy, or a carbon material intercalated with lithium; and
a nonaqueous electrolyte.

4. The nonaqueous secondary cell according to Claim 3, where said positive electrode comprises an active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is Mn, having the lattice constants: a_0 being in the range of 2.87 to 2.89 Å; c_0 being in the range of 14.15 to 14.25 Å; and the ratio in the diffraction peak intensity of the face (006) to the face (101) indicated by the hexagonal miller indices, i.e., (006)/(101) being not higher than 0.60; and the magnitude of a unit cell volume being in the range of 101 to 103 $Å^3$.

5. The nonaqueous secondary cell according to Claim 3, where said positive electrode comprises an active material represented by the general formula: $Li_yNi_{1-x}Me_xO_2$ where Me is Mn, having a magnitude of a unit cell volume of 101 to 103 $Å^3$.

6. A process for producing an active material for use in nonaqueous electrolyte secondary cells represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ comprising:
employing as starting materials an amount of a compound of divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of a nickel compound corresponding to the number of atomic moles of Ni indicated by 1-x, and an amount of a lithium compound corresponding to the number of atomic moles of Li indicated by y;
predrying said starting materials;
subjecting to first heat-treatment;
passing through a cooling stage to produce an intermediate; and
subjecting said intermediate to second heat-treatment at a different temperature from that in said first heat-treatment;
said heat-treatments being conducted in an oxidizing atmosphere.

7. The process for producing an active material represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$, where said oxidizing atmosphere is air.

8. The process for producing an active material represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$, where said oxidizing atmosphere is oxygen.

9. The process for producing an active material for use in nonaqueous electrolyte secondary cells represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq$

0.3 and $1.0 \leq y \leq 1.3$ according to Claim 6, where it comprises:

employing as starting materials an amount of a compound of divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of at least one nickel compound selected from the group consisting of $Ni(OH)_2$ and $NiCO_3$ corresponding to the number of atomic moles of Ni indicated by 1-x, and an amount of $LiNO_3$ hydrate corresponding to the number of atomic moles of Li indicated by y;

predrying said starting materials at 150 °C for 15 hours;

subjecting said dried materials to first heat-treatment of heat-treating at a temperature of 550 to 650 °C for 15 to 20 hours;

passing through normal temperature to produce an intermediate having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 3; and

subjecting said intermediate to the second heat-treatment of heat-treating at a temperature of 700 to 800 °C for 20 to 25 hours to produce an end product having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 2;

said heat-treatments being conducted in an oxidizing atmosphere of air or oxygen.

10. The process for producing an active material for use in nonaqueous electrolyte secondary cells represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ according to Claim 6, where it comprises:

employing as starting materials an amount of a compound of divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of at least one nickel compound selected from the group consisting of $Ni(OH)_2$ and $NiCO_3$ corresponding to the number of atomic moles of Ni indicated by 1-x, and an amount of Li_2CO_3 corresponding to the number of atomic moles of Li indicated by y;

predrying said starting materials at 150 °C for 15 hours;

subjecting said dried materials to first heat-treatment of heat-treating at a temperature of 650 to 750 °C for 15 to 20 hours;

passing through normal temperature to produce an intermediate having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 4; and

subjecting said intermediate to the second heat-treatment of heat-treating at a temperature of 800 to 900 °C for 20 to 25 hours to produce an end product having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 2;

said heat-treatments being conducted in an oxidizing atmosphere of air or oxygen.

11. The process for producing an active material for use in nonaqueous electrolyte secondary cells represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ according to Claim 6, where it comprises:

employing as starting materials an amount of a compound of divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of at least one nickel compound selected from the group consisting of $Ni(OH)_2$ and $NiCO_3$ corresponding to the number of atomic moles of Ni indicated by 1-x, and an amount of $LiNO_3$ hydrate corresponding to the number of atomic moles of Li indicated by y;

predrying said starting materials at 150 °C for 15 hours;

subjecting said dried materials to first heat-treatment of heat-treating at a temperature of 700 to 800 °C for 20 to 25 hours;

passing through normal temperature to produce an intermediate having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 5; and

subjecting said intermediate to the second heat-treatment of heat-treating at a temperature of 250 to 350 °C for 10 to 15 hours to produce an end product having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 2;

said heat-treatments being conducted in an oxidizing atmosphere of air or oxygen.

12. The process for producing an active material for use in nonaqueous electrolyte secondary cells represented by the general formula: $Li_yNi_{1-x}Mn_xO_2$ where the numbers of moles of x and y are $0 \leq x \leq 0.3$ and $1.0 \leq y \leq 1.3$ according to Claim 6, where it comprises:

employing as starting materials an amount of a compound of divalent manganese corresponding to the number of atomic moles of Mn indicated by x, an amount of at least one nickel compound selected from the group consisting of $Ni(OH)_2$ and $NiCO_3$ corresponding to the number of atomic moles of Hi

indicated by 1-x, and an amount of Li_2CO_3 corresponding to the number of atomic moles of Li indicated by y;

predrying said starting materials at 150 °C for 15 hours;

subjecting said dried materials to first heat-treatment of heat-treating at a temperature of 800 to 900 °C for 20 to 25 hours;

passing through normal temperature to produce an intermediate having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 6; and

subjecting said intermediate to the second heat-treatment of heat-treating at a temperature of 250 to 350 °C for 10 to 15 hours to produce an end product having the crystalline structure as identified by the X-ray diffraction pattern shown in Figure 2;

said heat-treatments being conducted in an oxidizing atmosphere of air or oxygen.

FIG. 1

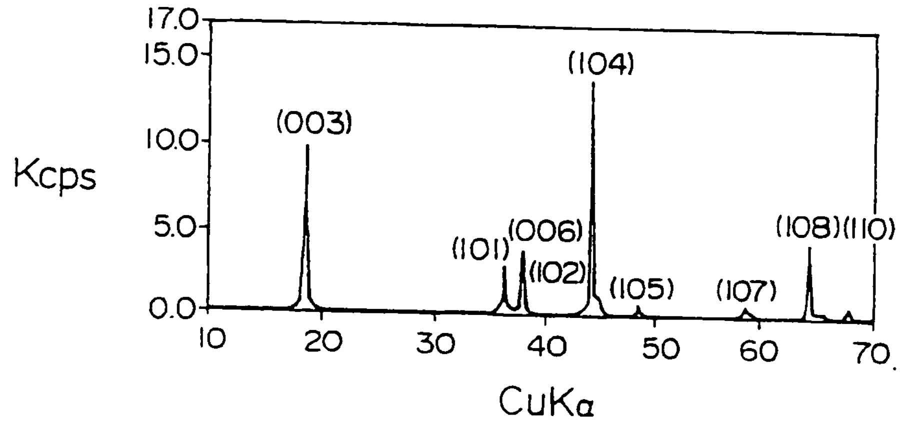


FIG. 2

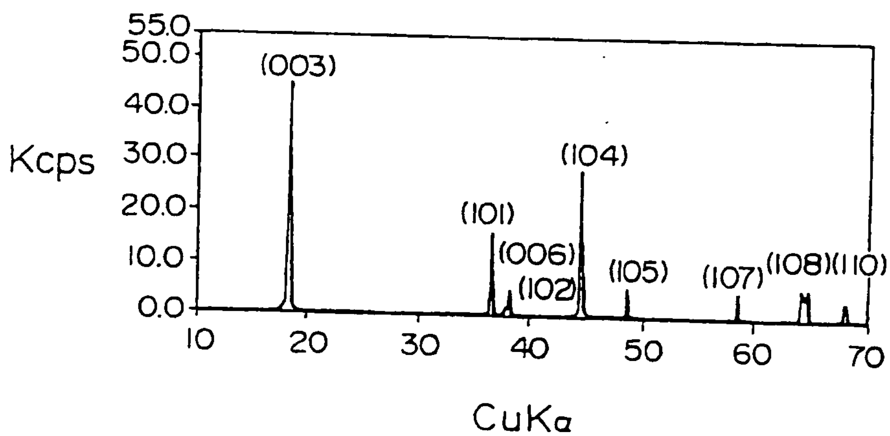


FIG. 3

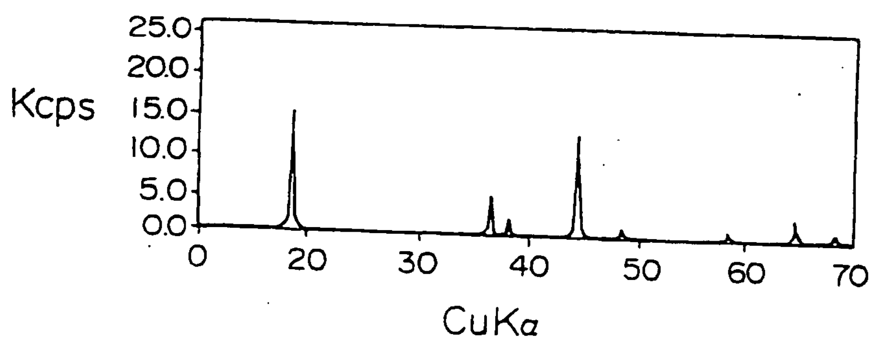


FIG. 4

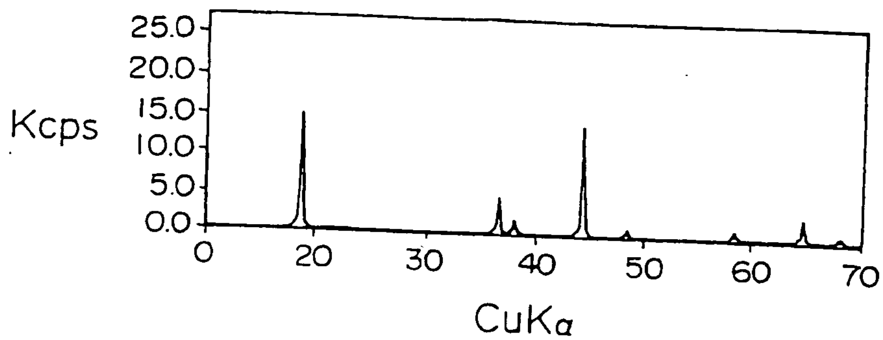


FIG. 5

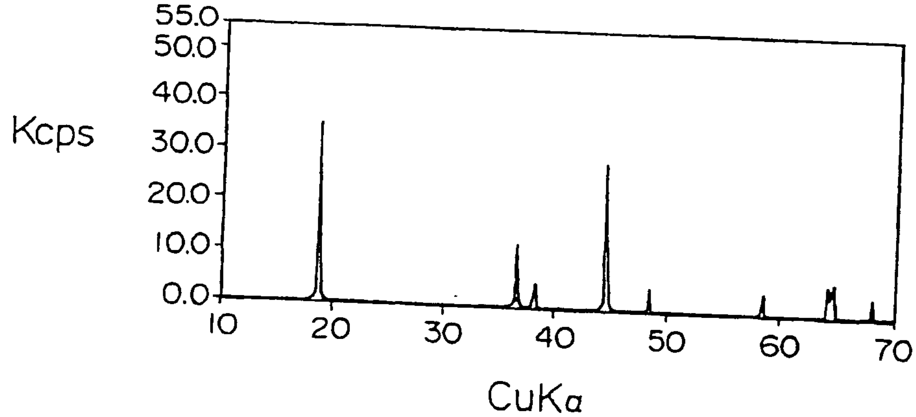


FIG. 6

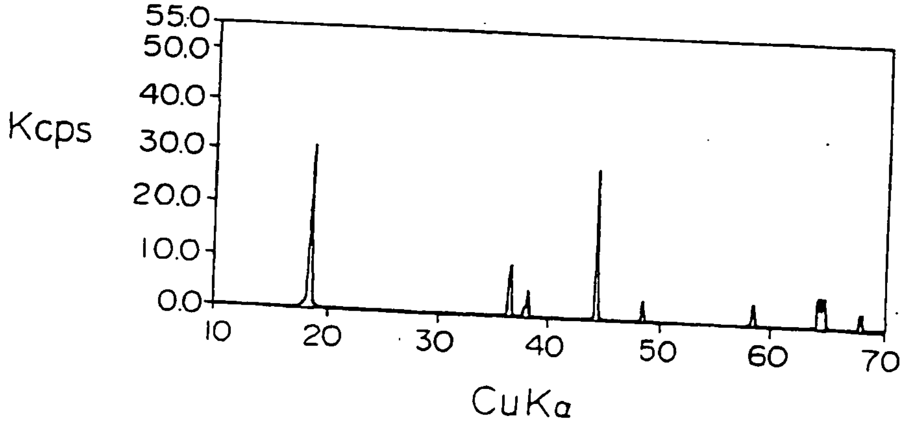


FIG. 7

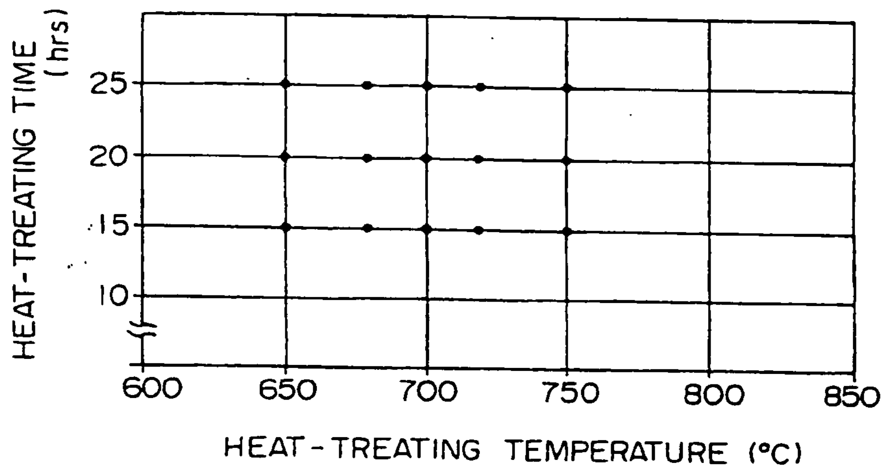


FIG. 8

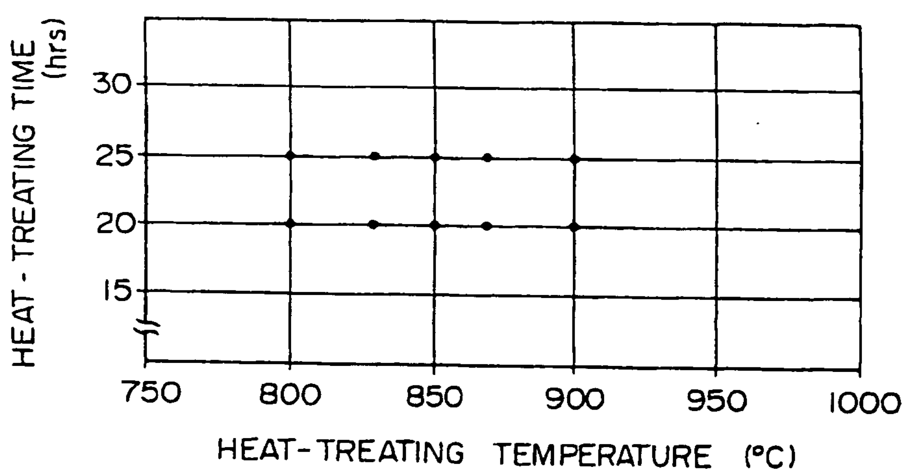


FIG. 9

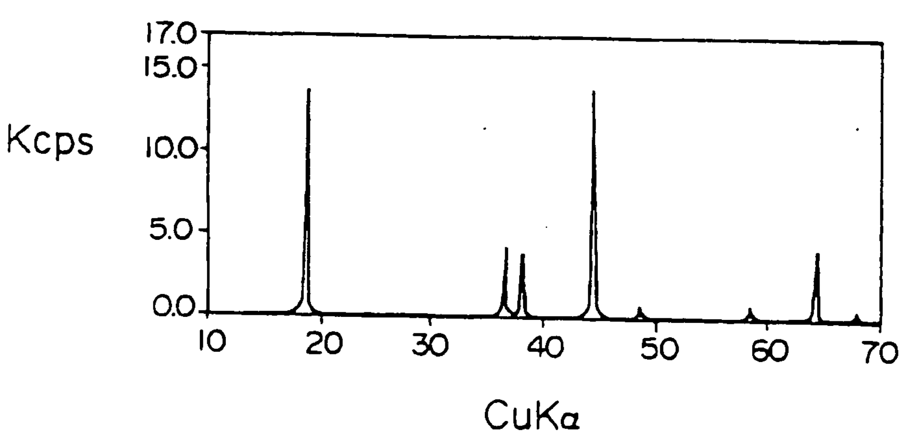


FIG. 10

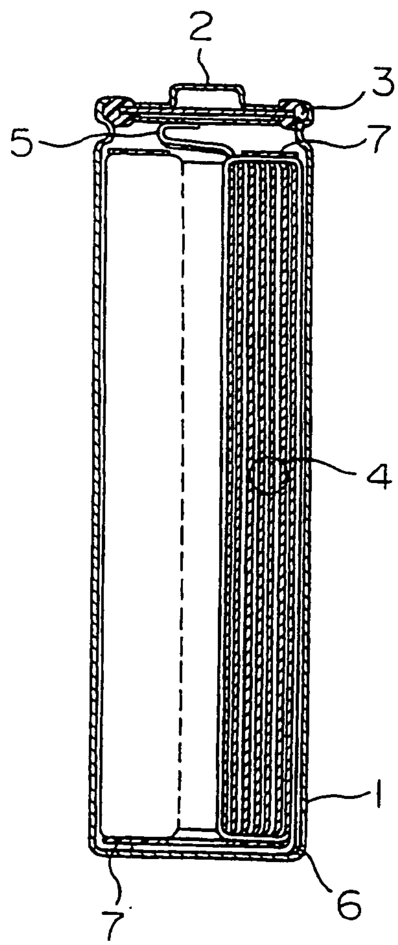
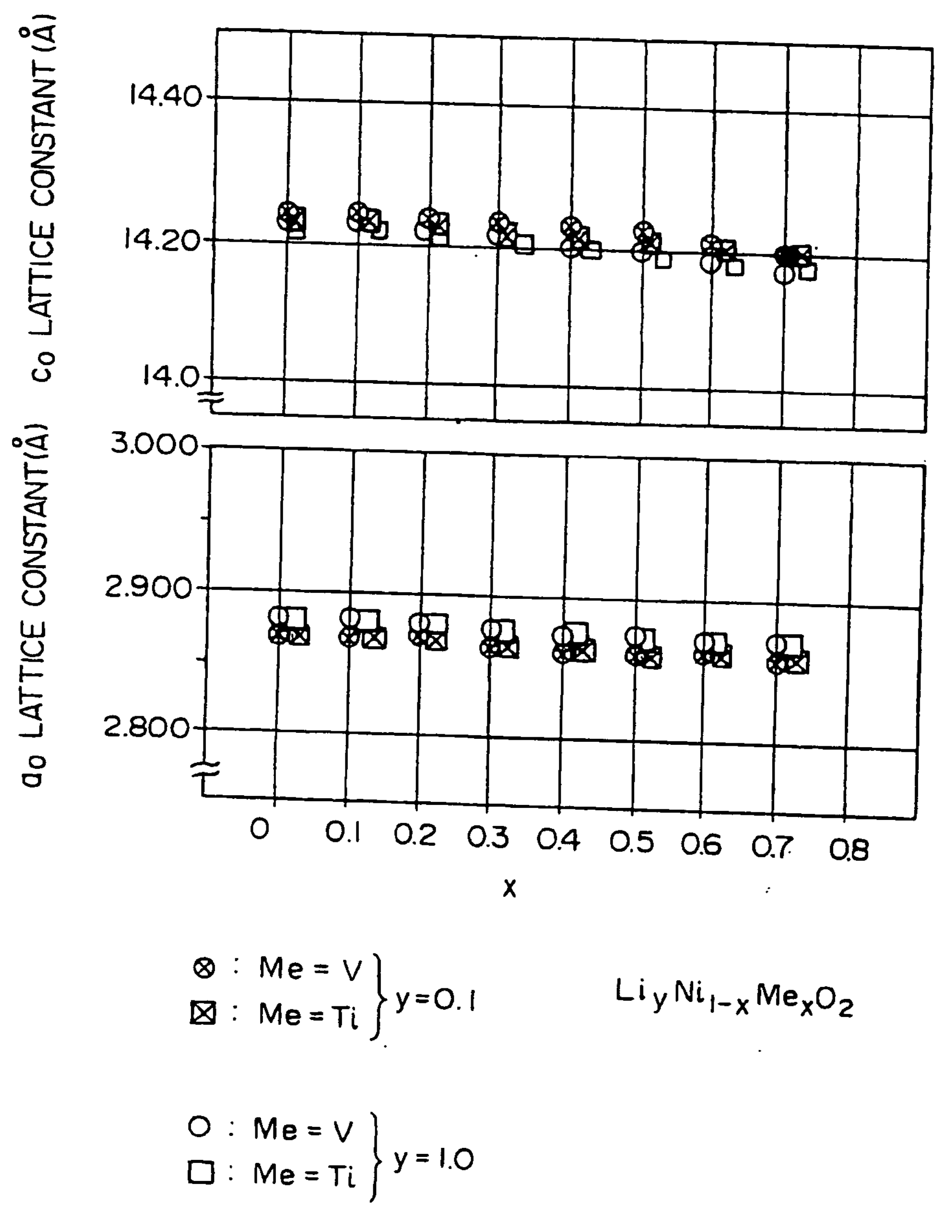


FIG. 11



c_0 LATTICE CONSTANT (Å)
14.40
14.20
14.0
a_0 LATTICE CONSTANT (Å)
3.000
2.900
2.800
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x
⊗ : Me = V
⊠ : Me = Ti
y = 0.1
○ : Me = V
□ : Me = Ti
y = 1.0
$Li_yNi_{1-x}Me_xO_2$

FIG. 12

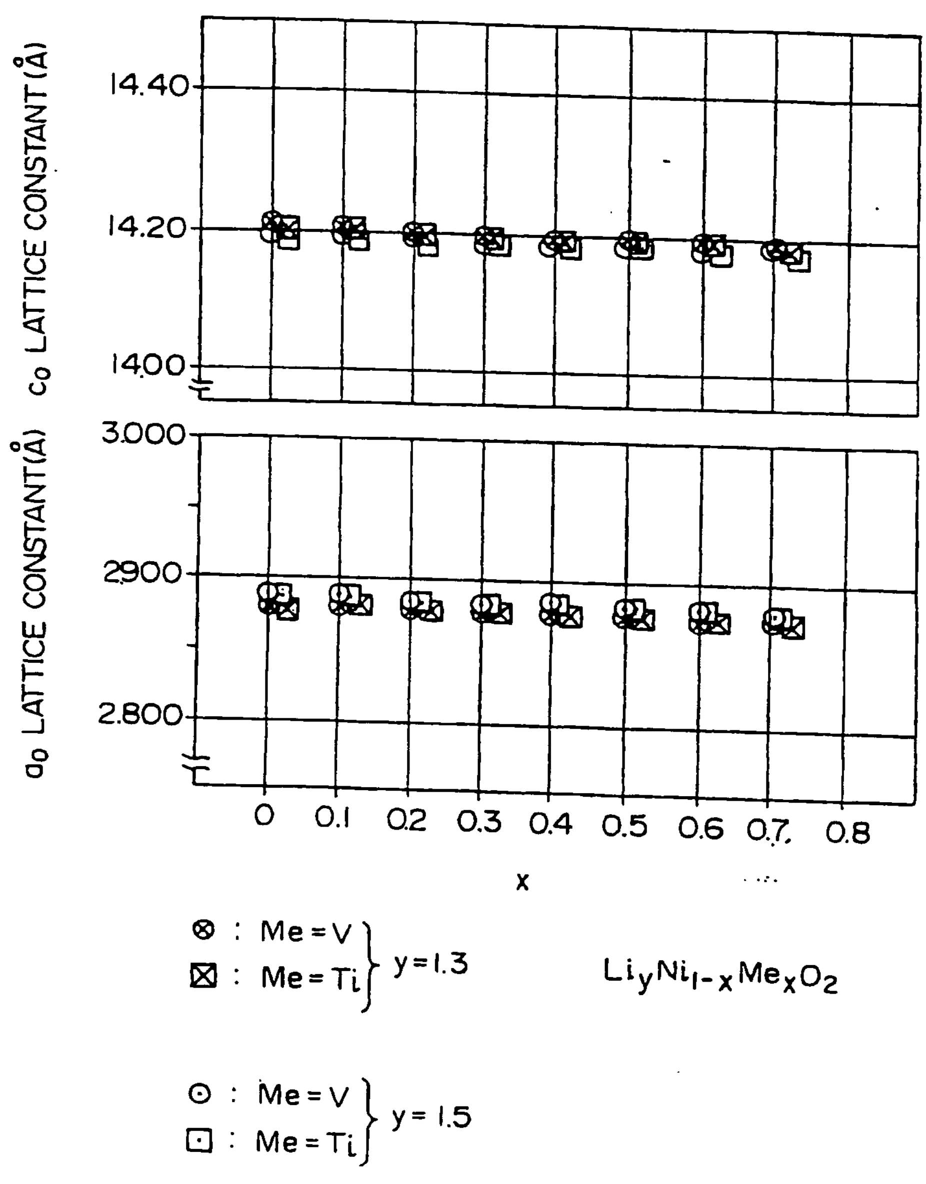

c_0 LATTICE CONSTANT (Å)
14.40
14.20
14.00
a_0 LATTICE CONSTANT (Å)
3.000
2.900
2.800
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x
⊗ : Me = V
⊠ : Me = Ti
y = 1.3
⊙ : Me = V
⊡ : Me = Ti
y = 1.5
$Li_yNi_{1-x}Me_xO_2$

FIG. 13

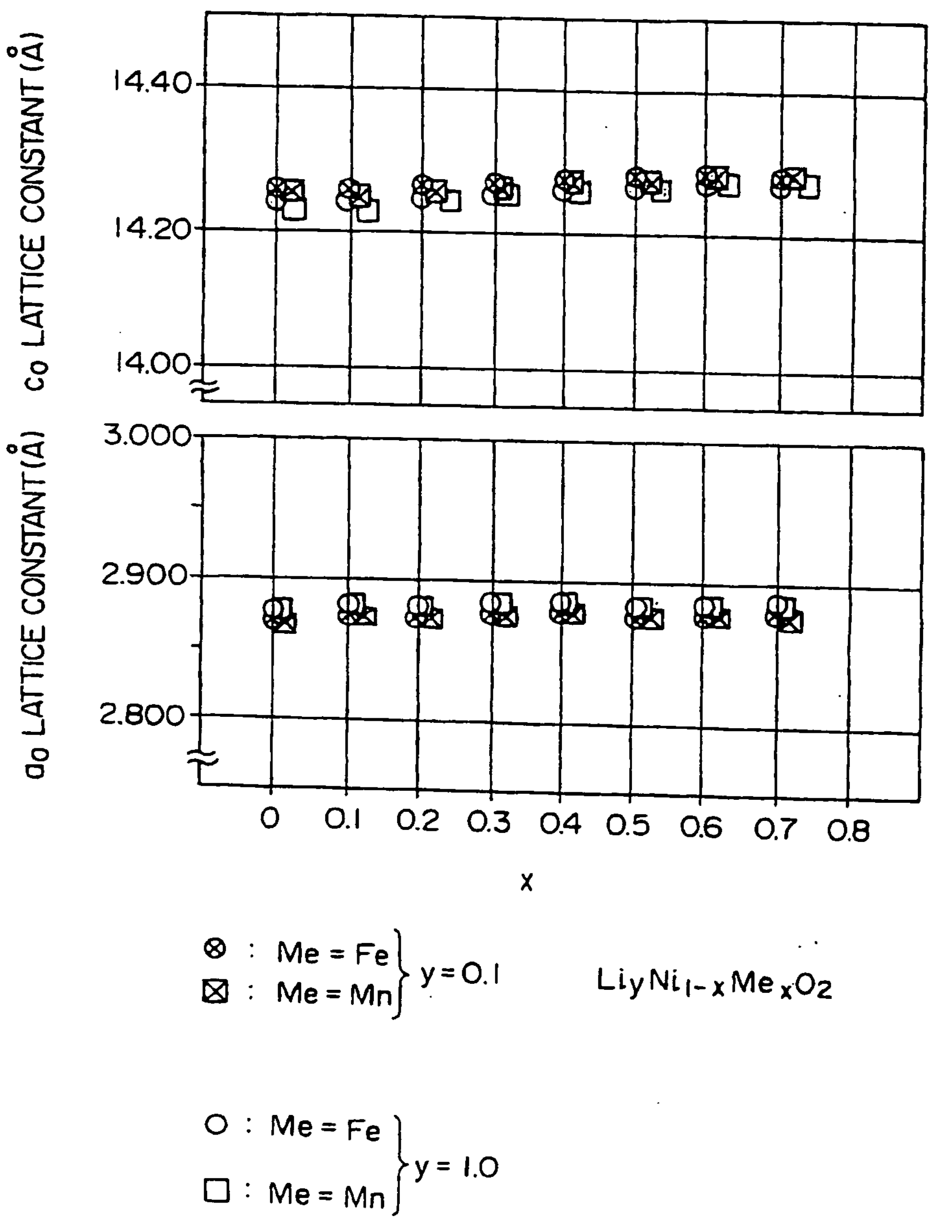

14.40
14.20
14.00
co LATTICE CONSTANT (Å)
3.000
2.900
2.800
ao LATTICE CONSTANT (Å)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x
⊗ : Me = Fe
⊠ : Me = Mn
y = 0.1
LiyNi1-xMexO2
○ : Me = Fe
□ : Me = Mn
y = 1.0

FIG. 14

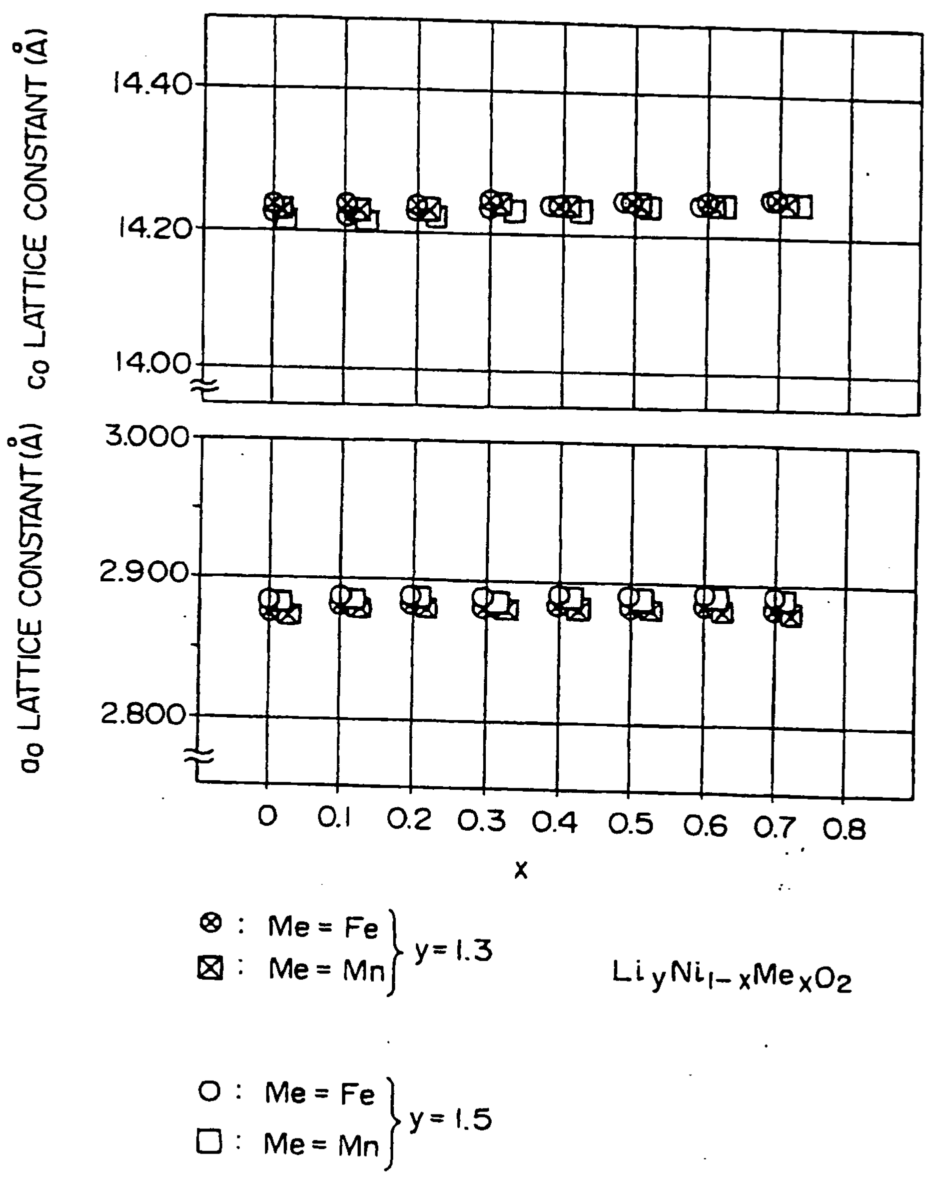

co LATTICE CONSTANT (Å)
14.40
14.20
14.00
ao LATTICE CONSTANT (Å)
3.000
2.900
2.800
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
x
⊗ : Me = Fe
⊠ : Me = Mn
y = 1.3
○ : Me = Fe
□ : Me = Mn
y = 1.5
$Li_yNi_{1-x}Me_xO_2$

FIG. 15

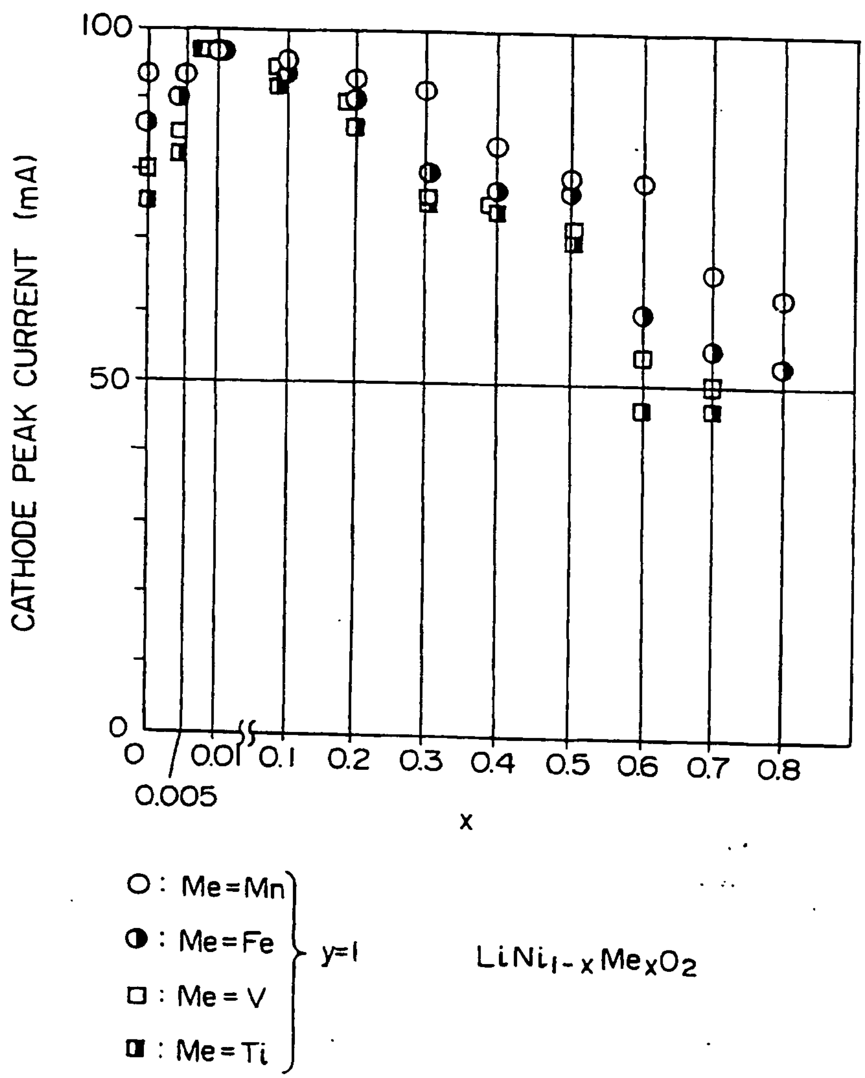

CATHODE PEAK CURRENT (mA)
100
50
0
0
0.005
0.01
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x
○ : Me=Mn
◑ : Me=Fe
□ : Me=V
◧ : Me=Ti
y=1
$LiNi_{1-x}Me_xO_2$

FIG. 16

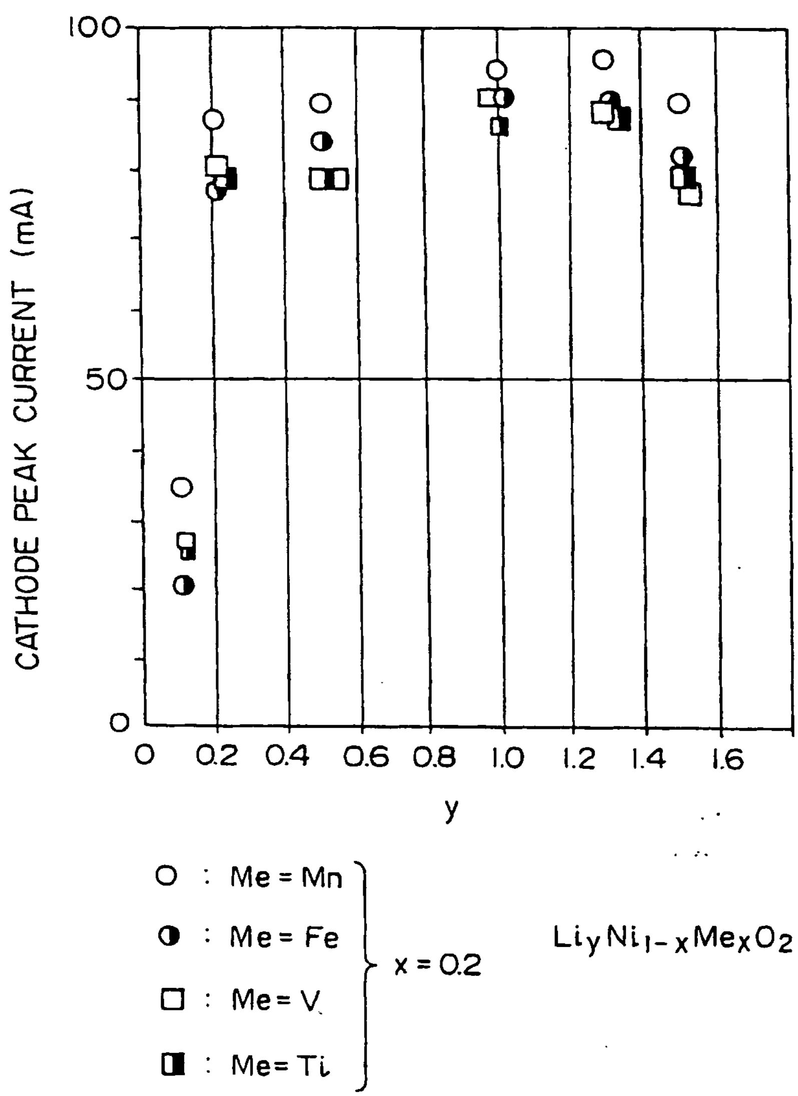

100
50
0
CATHODE PEAK CURRENT (mA)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
y
: Me = Mn
: Me = Fe
: Me = V
: Me = Ti
x = 0.2
$Li_yNi_{1-x}Me_xO_2$

FIG. 17

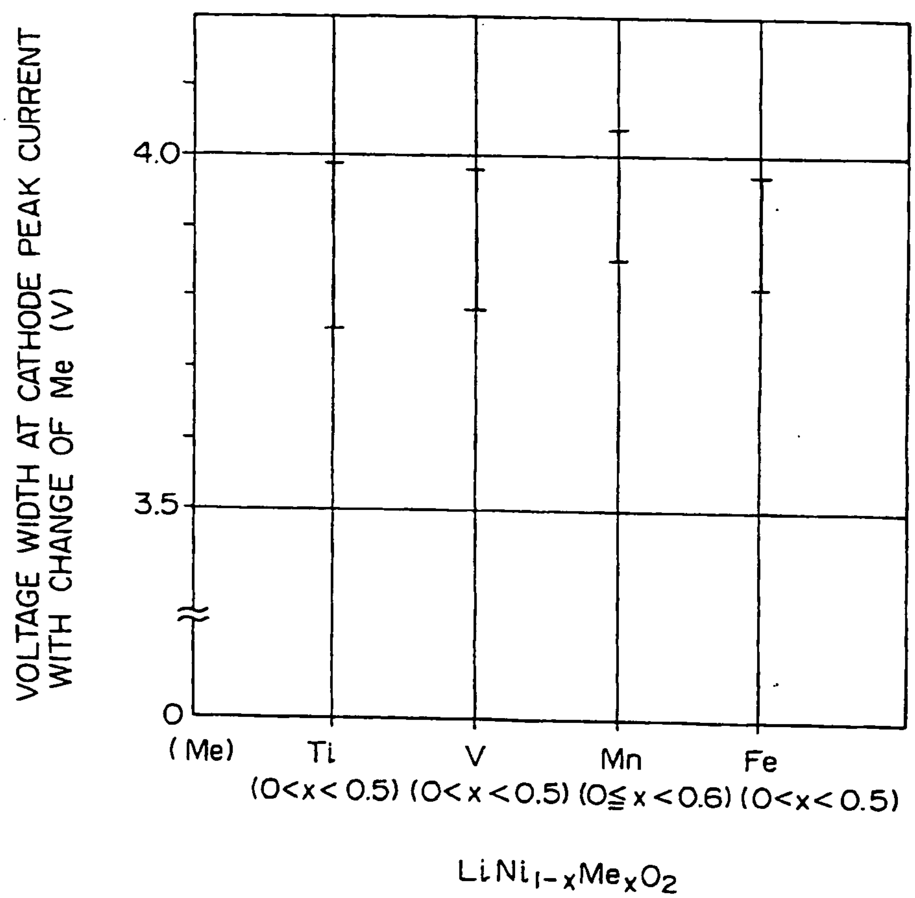

VOLTAGE WIDTH AT CATHODE PEAK CURRENT
WITH CHANGE OF Me (V)
4.0
3.5
0
(Me)
Ti
(0<x< 0.5)
V
(0<x<0.5)
Mn
(0≦x<0.6)
Fe
(0<x<0.5)
$LiNi_{1-x}Me_xO_2$

FIG. 18

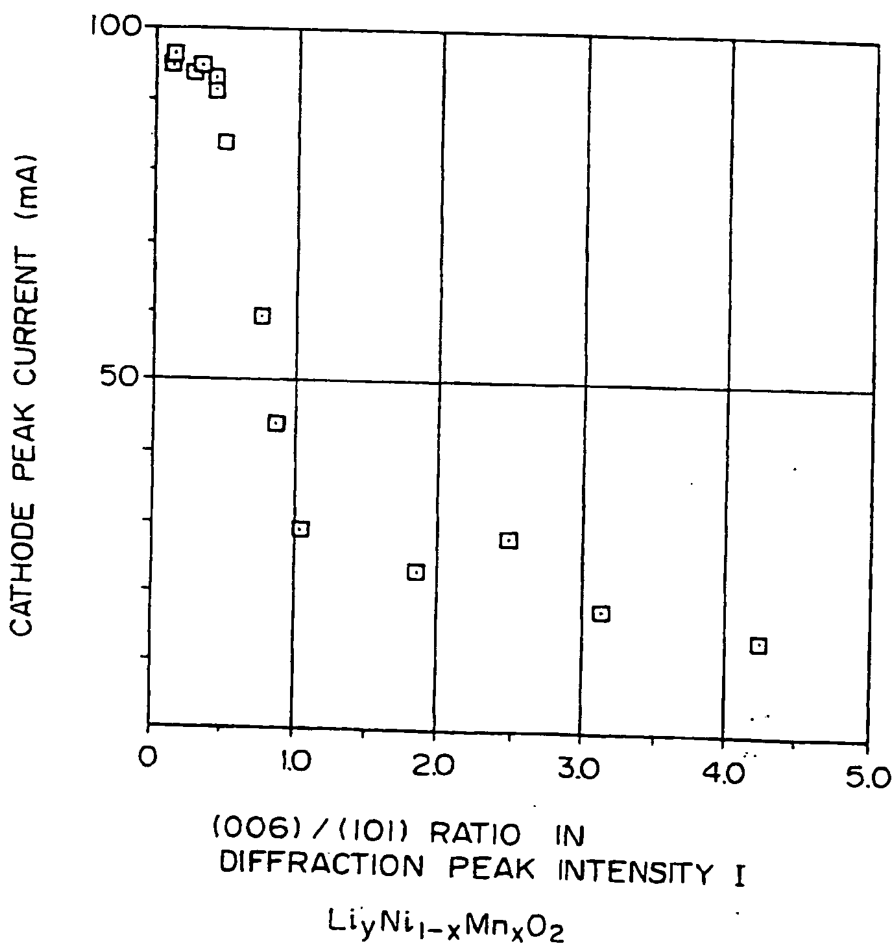
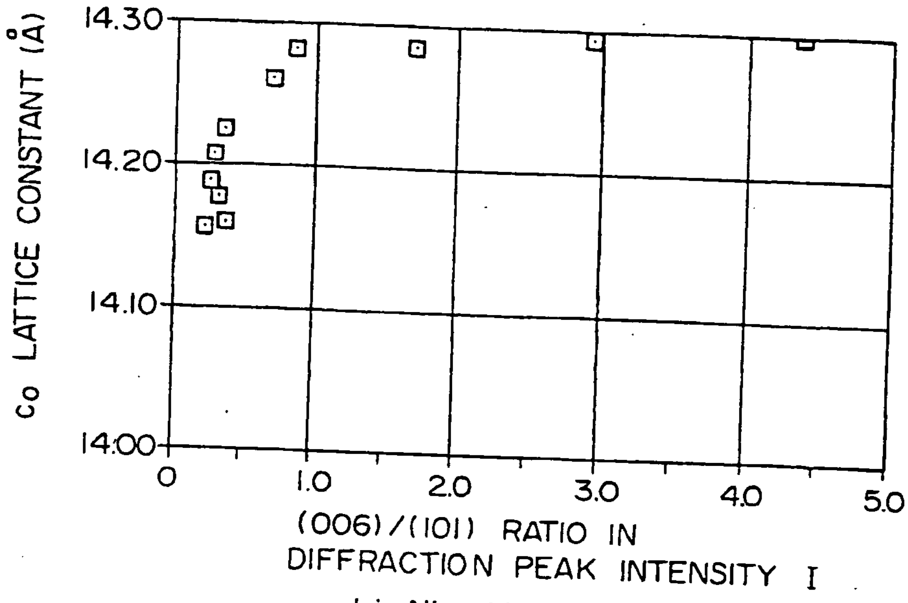

100
50
CATHODE PEAK CURRENT (mA)
0
1.0
2.0
3.0
4.0
5.0
(006) / (101) RATIO IN
DIFFRACTION PEAK INTENSITY I
$Li_yNi_{1-x}Mn_xO_2$

FIG. 19



$Li_yNi_{1-x}Mn_xO_2$

FIG. 20

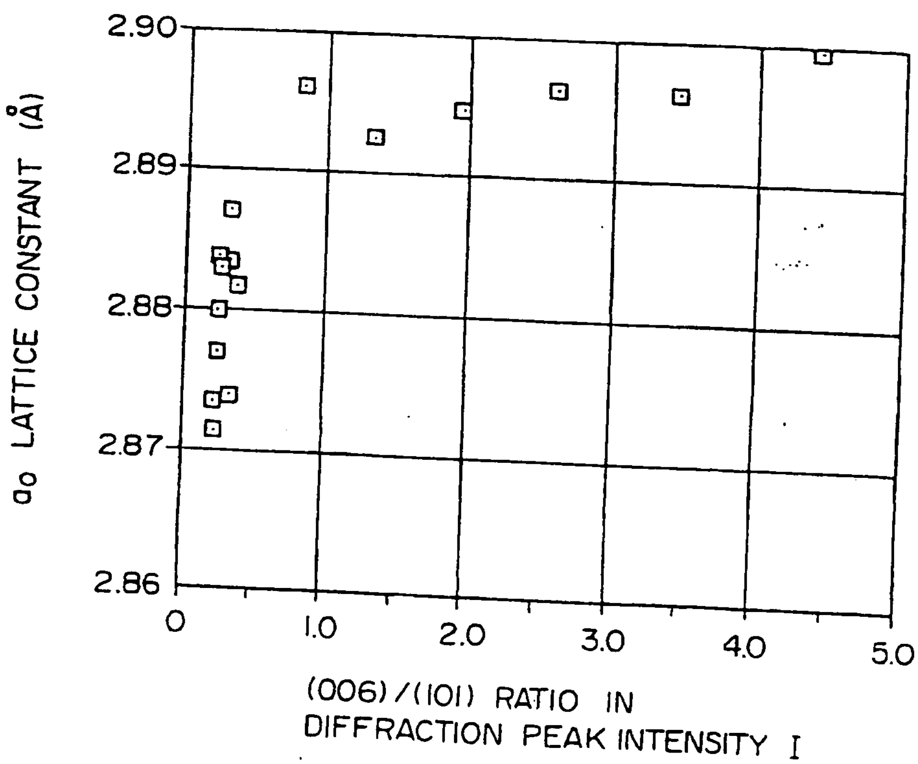
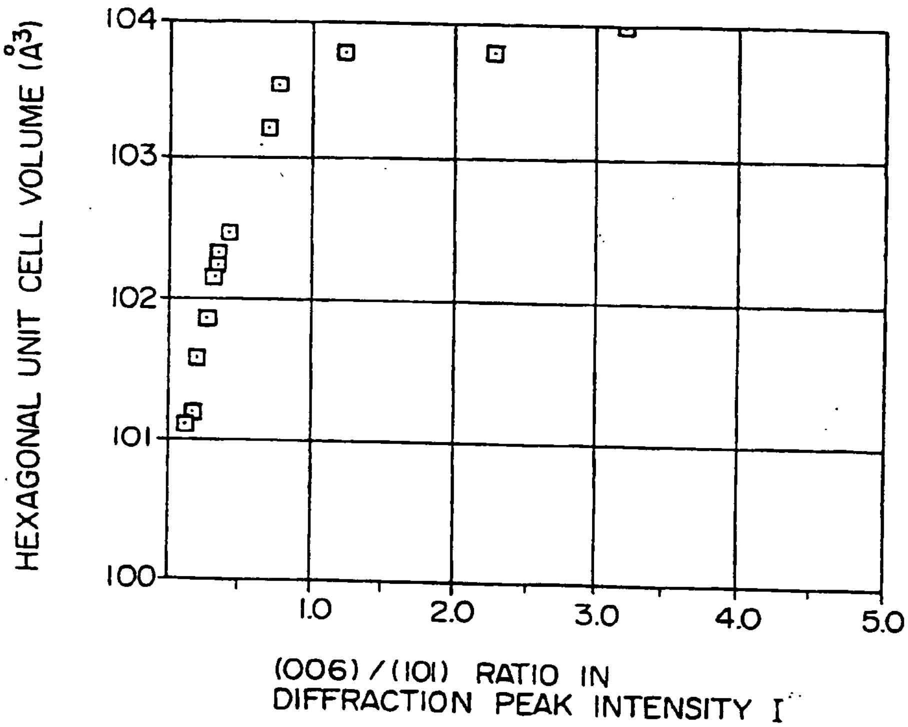


FIG. 21



$Li_yNi_{1-x}Mn_xO_2$

FIG. 22

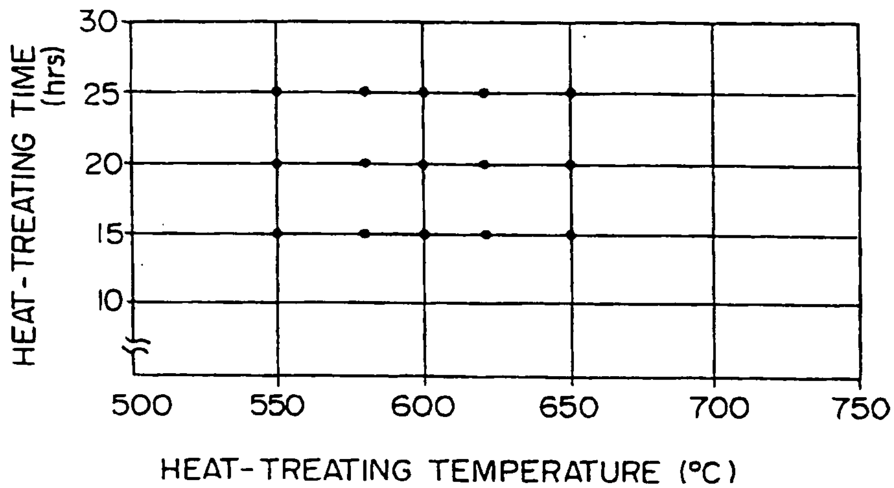

HEAT-TREATING TIME (hrs)
30
25
20
15
10
500
550
600
650
700
750
HEAT-TREATING TEMPERATURE (°C)

FIG. 23

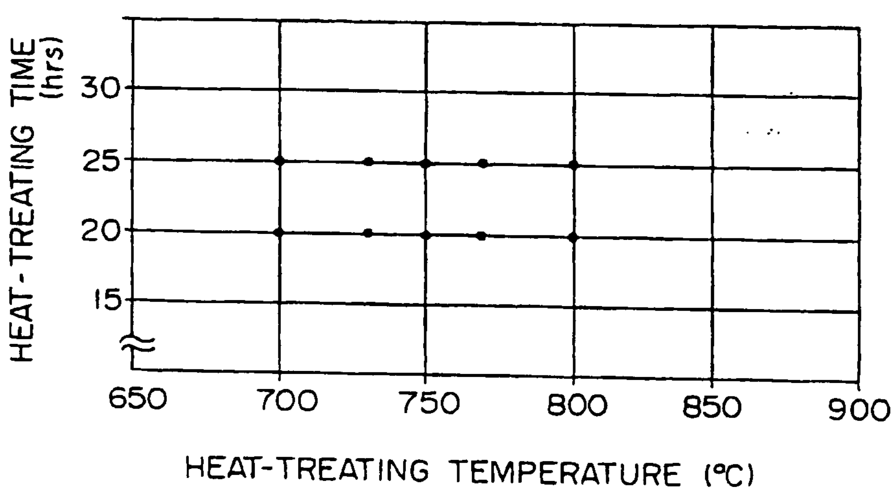

HEAT-TREATING TIME (hrs)
30
25
20
15
650
700
750
800
850
900
HEAT-TREATING TEMPERATURE (°C)

FIG. 24

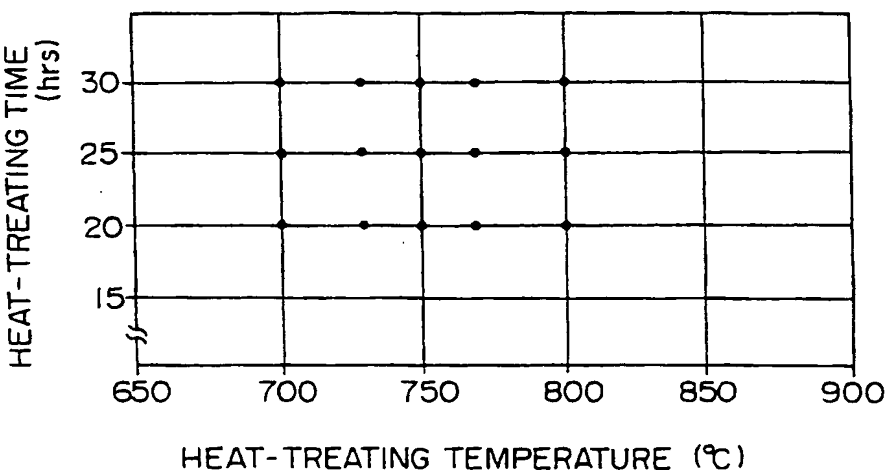

HEAT-TREATING TIME (hrs)
30
25
20
15
650
700
750
800
850
900
HEAT-TREATING TEMPERATURE (°C)

FIG. 25

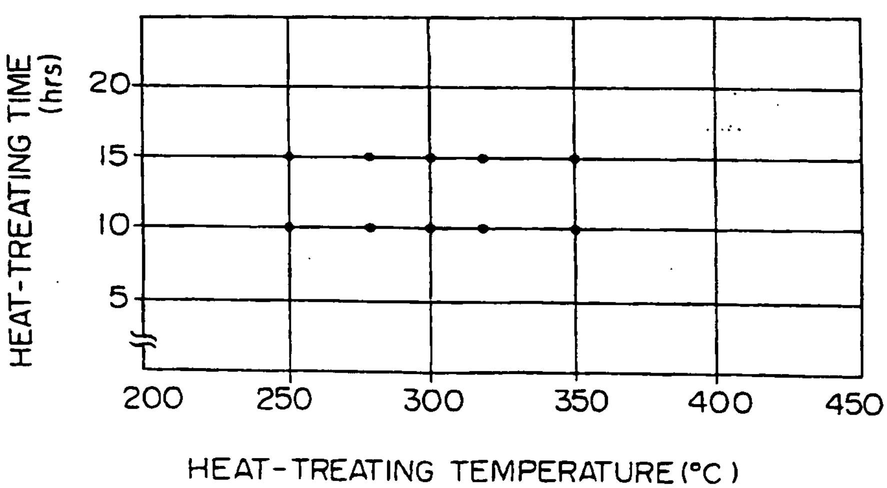

HEAT-TREATING TIME (hrs)
20
15
10
5
200
250
300
350
400
450
HEAT-TREATING TEMPERATURE (°C)

FIG. 26

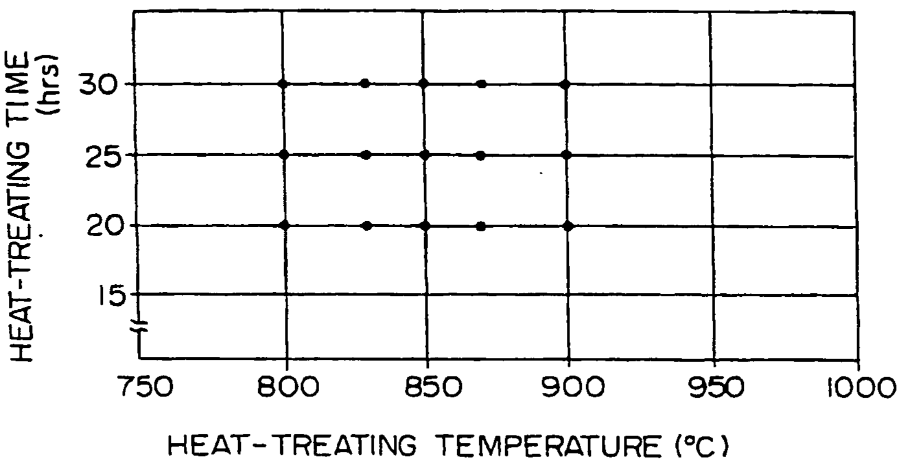

HEAT-TREATING TIME (hrs)
30
25
20
15
750
800
850
900
950
1000
HEAT-TREATING TEMPERATURE (°C)

FIG. 27

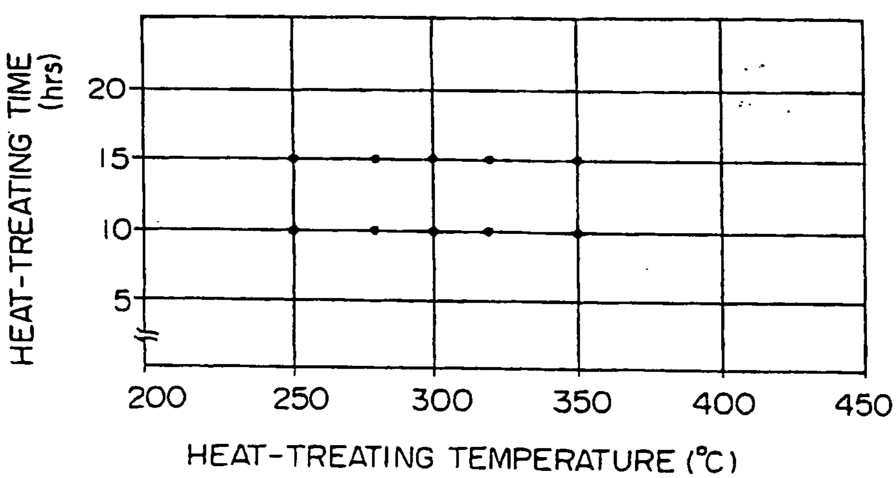
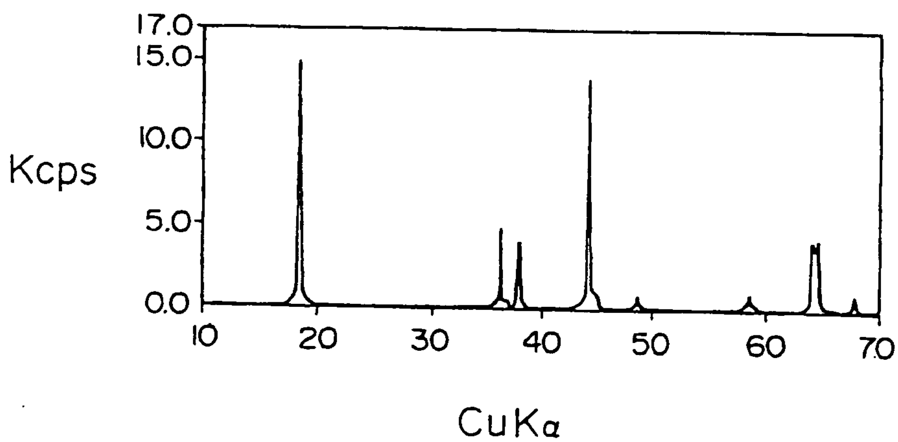

HEAT-TREATING TIME (hrs)
20
15
10
5
200
250
300
350
400
450
HEAT-TREATING TEMPERATURE (°C)

FIG. 28



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 1859

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	EP-A-0 468 942 (HER MAJESTY THE QUEEN) * claims 1,24 * * page 9; example 1 * -----	1-3,7	H01M4/48 C01G53/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			H01M C01G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 JUNE 1993	M. P. ANDREWS

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document